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CHEMICAL DURABILITY IMPROVEMENT AND STATIC FATIGUE OF GLASSES.(U)  
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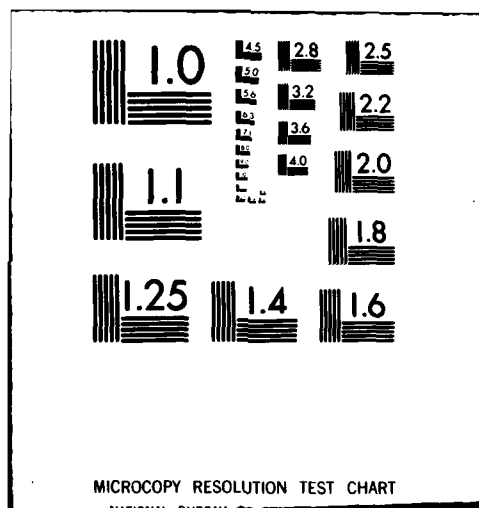
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# I. SUMMARY

-Chemical durability of glass can be improved by applying a coating on the surface. It was also found that an addition of a minor quantity of calcium to the alkaline solution drastically improves the durability of silica glass. It was confirmed that calcium produces a film on the glass surface and protects the glass. A systematic study was made on the effects of all alkaline earth elements to see whether a similar phenomenon exists. All the alkaline earth elements were found to produce films, to a varied degree, on silica glass surface in alkaline solution. In addition, extensive crack growth was observed in the case of heavy alkaline earth elements such as Ba and Sr.

The strength of glass is strongly influenced by the environment in which it is measured, but the exact cause of the phenomenon is not clear. Usually, the phenomenon is explained by the stress-corrosion mechanism which suggests the corrosion rate increases with increasing tensile stress. Preliminary data on the hydrostatic pressure dependence of the dissolution rate of silica glass indicated the opposite trend; the higher dissolution rate at higher compressive stress.

Mechanical strength of high silica glass was measured in various liquids, as a function of stress rate. At a constant stress rate, the strength of glass measured in various liquids correlated well with the surface energy of the glass estimated from the volume change of a high silica porous glass immersed in various liquids. These observations suggest that the surface energy produces the mechanical stress which influences the mechanical strength of glass. Several possible mechanisms by which the surface energy affects the

mechanical strength of glass were considered. Stress rate dependence of strength of glass was reduced when the surface hydroxyl, which is usually considered the site of physical adsorption of water, is removed completely, while it remained unchanged when the surface hydroxyl is removed incompletely.

## II. RESEARCH AND RESULTS

### 1. Chemical Durability Improvement

In the course of the investigation of the effect of coating on the chemical durability of glass, it was found that addition of a minor quantity of calcium to the alkaline solution has a drastic effect in reducing the etching rate of  $\text{SiO}_2$  glass. It was established that calcium forms a film on the glass surface and reduces the etching rate. A systematic study was made on the effect of all alkaline earth elements on the alkaline durability of  $\text{SiO}_2$  glass to see whether a similar phenomenon is observed. The surface film formation was recognized for all the alkaline earth elements, to a varied degree, while no film formation was observed when Al or Zn was added to alkaline solution (Appendix I). In addition, extensive crack growth was observed when high silica glass was exposed to alkaline solution containing heavy alkaline earth elements such as Ba or Sr. The mechanical strength of the resulting glass rods was extremely low, being only 1/4 of the original strength (Appendix II). This phenomenon can pose a serious problem in the application of high silica glass fibers to optical wave guide.

### 2. Environmental Effect on Mechanical Strength of Glass

Mechanical strength of glass is strongly influenced by the environment in which it is measured. For example, the strength measured in water is lower than that measured in vacuum at a constant stress rate. One explanation

of this phenomenon is in terms of the chemical reaction between the glass and the environment. This mechanism is based upon the hypothesis that the chemical reaction is accelerated under tensile stress, but there is no direct experimental evidence for it. Our preliminary investigation of dissolution rate of silica glass in water in hydrostatic pressure showed the opposite trend; the dissolution rate increased with increasing hydrostatic pressure (compressive stress) (Figure 1).

Another mechanism suggested is the lowering of the fracture surface energy in the Griffith equation. However, the cause of the lowering of the fracture surface energy is not clear.

The objective of the research, here, is to find out the real cause of the environmental effect on the mechanical strength of glass. First, the mechanical strength of a high silica glass was measured in various organic liquids as a function of stress rate. Since water is known to have the greatest influence on the mechanical strength of glass, all the organic liquids were treated with molecular sieves to eliminate the trace amount of water. The mechanical strength in a liquid at a given stress rate showed a good correlation with the resultant surface energy of the glass in the liquid (Appendix III). Several mechanisms by which the surface energy influences the mechanical strength of glass were considered (Appendix IV). One possible mechanism is the alteration of radius of curvature at the crack tip by the surface energy.

The surface energy of glass is changed by physical adsorption of various molecules on the surface hydroxyl. Attempts were made to change the concentration of the surface hydroxyl and see its effect on the mechanical strength,

especially the stress rate dependence. Figure 2 shows a part of the result; the stress rate dependence of high silica glass in  $\text{CH}_3\text{SiCl}_3$  solution is the same as that in water while practically no stress rate dependence is recognized for specimens in Grignard reagent. It is believed that in  $\text{CH}_3\text{SiCl}_3$  solution most of the hydroxyl is replaced by  $\text{O}-\overset{\cdot}{\text{Si}}-\text{CH}_3$ , but some hydroxyl remains on the glass surface. On the other hand, in Grignard reagent ( $\text{CH}_3\text{MgBr}$ ) solution, the surface hydroxyl is quantitatively replaced by  $\text{O}-\text{MgBr}$ . These results clearly indicate that the surface hydroxyl, which is the site of physical adsorption of water, plays an important role in determining the fatigue characteristics of glass. The observed phenomenon appears to offer an important clue to the environmental effect of the mechanical strength of glass.

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### IV. PUBLICATIONS

- "Swelling and Mechanical Strength of Glass", Y. Oka, J.M. Wahl and M. Tomozawa, J. Non-Crystalline Solids 38/39 397 (1980).



- "Effect of Alkaline Earth Ion As An Inhibitor to Alkaline Attack on Silica Glass", J. Non-Crystalline Solids 42 535 (1980).
- "Glass Surface Cracks Caused by Alkaline Solution Containing Alkaline Earth Element", M. Tomozawa, Y. Oka and J.M. Wahl. To appear in Comm. Am. Ceram Soc.
- "Environmental Effect on the Mechanical Strength of Glass", M. Tomozawa and Y. Oka. To appear in the Proceedings of the 17th University Conference on Ceramics.
- "Effect of Surface Energy on the Mechanical Strength of a High Silica Glass". Submitted to J. Am. Ceram. Soc.

#### V. ORAL PRESENTATIONS

- "Swelling and Mechanical Strength of Glass", Y. Oka, J.M. Wahl, and M. Tomozawa, XII International Congress on Glass, Albuquerque, N.M. July, 1980.
- "Effect of Alkaline Earth Ion As A Inhibitor To Alkaline Attack on Silica Glass", Y. Oka and M. Tomozawa. Frontier of Glass Science, An International Conference, Los Angeles, CA. July 1980.
- "Environmental Effect on the Mechanical Strength of Glass", M. Tomozawa and Y. Oka", 17th University Conference on Ceramics. Berkeley, CA, August, 1980.

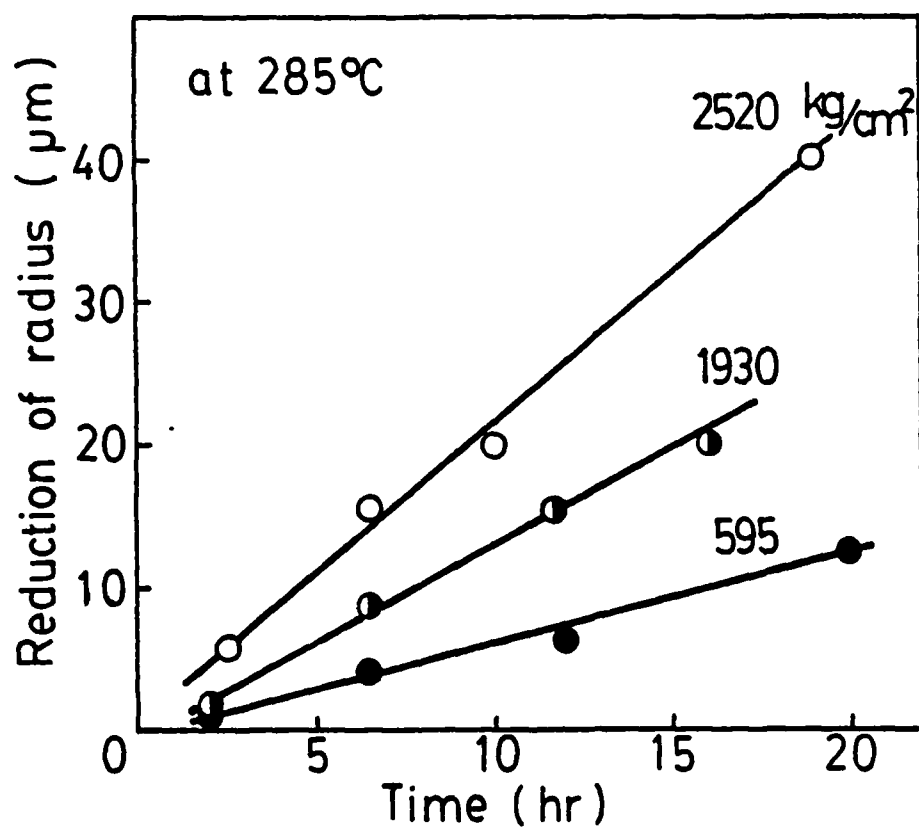


Figure 1: Dissolution rate of  $\text{SiO}_2$  glass as a function of hydrostatic pressure in a hydrothermal unit. Dissolution rate was determined by measuring the weight loss.

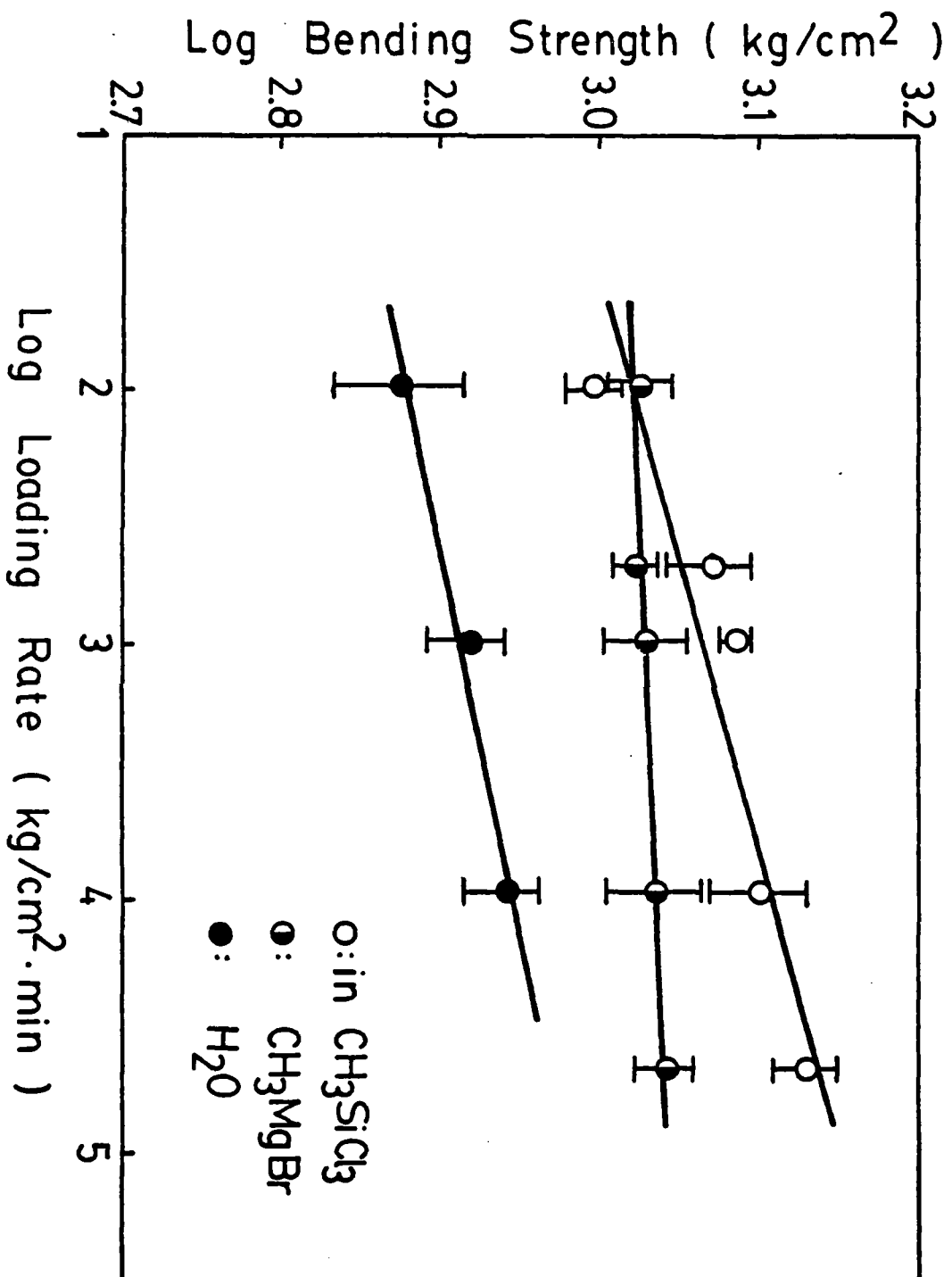


Figure 2: Stress rate dependence of mechanical strength of high silica glass in various solution.

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surface in alkaline solution. In addition, extensive crack growth was observed in the case of heavy alkaline earth elements such as Ba and Sr.

The strength of glass is strongly influenced by the environment in which it is measured, but the exact cause of the phenomenon is not clear. Usually, the phenomenon is explained by the stress-corrosion mechanism which suggests the corrosion rate increase with increasing tensile stress. Preliminary data on the hydrostatic pressure dependence of the dissolution rate of silica glass indicated the opposite trend; the higher dissolution rate at higher compressive stress.

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## Appendix I

### EFFECT OF ALKALINE EARTH ION AS AN INHIBITOR TO ALKALINE ATTACK ON SILICA GLASS

Y. Oka and M. Tomozawa

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Rensselaer Polytechnic Institute  
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Inhibitor action of Be, Mg, Ca, Sr, Ba, Zn and Al to the alkaline solution attack on silica glass was investigated. Metal silicate hydrated compound was formed on silica glass surface when a minute quantity of alkaline earth element was added to sodium hydroxide solution, while no such film was formed when Zn or Al was added. In addition, extensive crack growth was observed in the case of heavy alkaline earth elements such as Ba and Sr.

#### INTRODUCTION

Oxide glasses are attacked by aqueous alkaline solutions which dissolve the glass network [1]. A small amount of certain metal ions in the alkaline solution has an effect to reduce the rate of the attack. For example, Hudson and Bacon [2] observed that various metal ions reduced the alkaline attack of soda-lime glass, the most effective element being beryllium. Furuichi and Uno [3] reported that aluminate and zincate ions suppressed the alkaline attack of a sheet glass and that the higher concentration of the additive had the greater effect. However, the mechanism by which impurity metal ions in solution reduce the alkaline corrosion rate of glass remains unclear.

Present authors investigated the effect of a small amount of calcium in alkaline solution on silica glass corrosion and reported [4] that calcium was deposited on the glass surface. In the present work the investigation was extended to a series of alkaline earth elements as well as zinc and aluminum, which are known to have the inhibitor effect on the alkaline corrosion of glass, with the objective to clarify the mechanism of corrosion inhibition.

#### EXPERIMENTAL

Silica microscope slide glass<sup>1</sup> was used for etching experiments to avoid possible effects of unintended ions which might come into the solution from glass. A glass sample was treated in 150ml of 1N NaOH solution with and without additives such as 0.001 mol/l of BeCO<sub>3</sub>, MgCl<sub>2</sub>, CaCl<sub>2</sub>, SrCl<sub>2</sub>, BaCl<sub>2</sub>, ZnCl<sub>2</sub> or AlCl<sub>3</sub>.

Porous glass<sup>2</sup> with high surface area ( $\sim 135\text{m}^2/\text{g}$ ) [5] was used to study the deposition of calcium on glass surface. Porous glass was crushed into small particles (20 to 35 mesh), etched with 5% HF for 5 minutes and dried in an oven at 400°C to remove any organic residue. Different weights of porous glass were immersed in 100ml of NaOH solutions with various concentrations. Calcium chloride (0.01 mol/l) was added to each solution and the solution was heated in an oven at 80°C for 2 hours. A preliminary experiment established that 2 hours is sufficient to establish the equilibrium. The solution was cooled in ice and filtered. The amount of calcium remained in the solution was determined by atomic absorption analysis.

For the silica surface analysis, ellipsometric measurement was carried out to obtain the thickness and refractive index of surface film [6]. Rudolph 436 Ellipsometer<sup>5</sup> was used on silica slide glass at the incidence angle of  $60^\circ$  and the wavelength of  $6328\text{\AA}$ . Ellipsometric parameters were determined to  $+0.15^\circ$  for  $\Delta$  and  $+0.04^\circ$  for  $\Psi$ . In addition, the silica glass surface was examined by SLM AMR1000.<sup>4</sup> X-ray diffraction analysis of surface corrosion product was also conducted.

## RESULTS

### 1. Etching Experiment

Figure 1(a) shows the weight loss of silica slide glass in 1N NaOH solution at  $80^\circ\text{C}$  when with and without  $0.001\text{ mol/l}$   $\text{AlCl}_3$ ,  $\text{ZnCl}_2$  addition. Al and Zn reduce the etching rate to the same extent and both show a straight line in etching amount vs. time. Figure 1(b) shows the results of the etching experiment for alkaline earth elements. It is noted that etching amount vs. time lines show a curvature for Ca, Be and Sr while it shows a straight line for Ba and Mg. The order in the reduction of the etching rate is Ca, Be, Sr, Mg and Ba after extended treatment time, while the order is reversed for Ca and Be in a short treatment time.

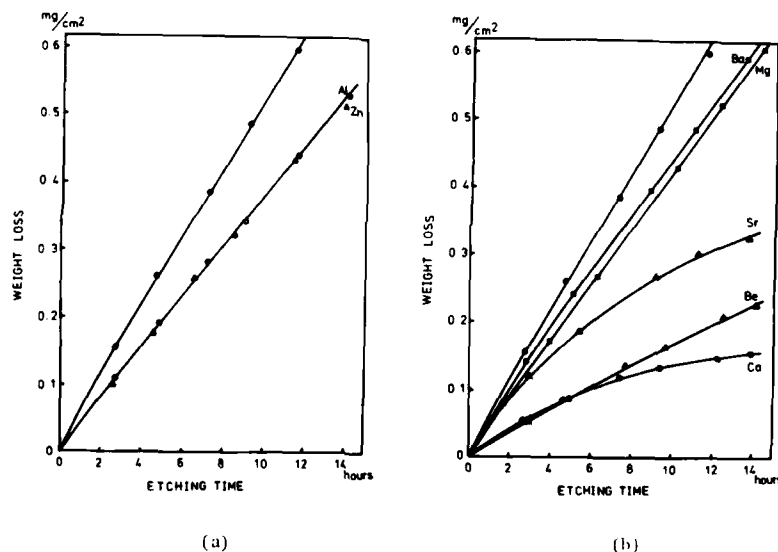


Figure 1

Weight loss vs. etching time on silica slide glass. The glass was treated at  $80^\circ\text{C}$  in 1N NaOH with  $0.001\text{ mol/l}$   $\text{AlCl}_3$  and  $\text{ZnCl}_2$  (a),  $\text{BeCl}_2$ ,  $\text{MgCl}_2$ ,  $\text{CaCl}_2$ ,  $\text{SrCl}_2$  and  $\text{BaCl}_2$  (b). Closed circle is for plain 1N NaOH.

### 2. Ca Deposition

Figure 2(a) shows the deposition of Ca on porous glass surface which has the composition of 96%  $\text{SiO}_2$ . In this figure,  $C_0$  and  $C$  denote the concentration of

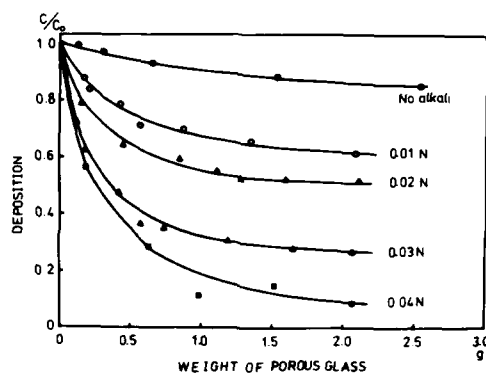


Figure 2 (a)

Calcium deposition vs. weight of porous glass. The glass was treated in 100ml of NaOH solution with 0.01 mol/l.  $\text{CaCl}_2$  at  $80^\circ\text{C}$  for 2 hours.

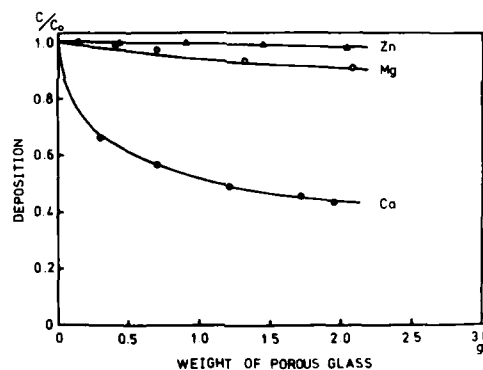


Figure 2 (b)

Deposition vs. weight of porous glass for Ca, Mg and Zn. The glass was treated in 0.001 mol/l.  $\text{CaCl}_2$ ,  $\text{MgCl}_2$  and  $\text{ZnCl}_2$  solutions at  $80^\circ\text{C}$  for 2 hours.

calcium in the solution before and after treatment, respectively. The weight of porous glass is proportional to the surface area. As is seen from this figure, Ca deposition was enhanced by increasing the alkalinity of the solution. Figure 2(b) shows the Ca, Mg and Zn depositions from distilled water containing 0.001 mol/l of respective metal chloride. The deposition of Ca is greater than Mg deposition and Zn does not show a measurable deposition.

## 3. Ellipsometric Measurement

In Table 1, ellipsometric parameters are listed, which were obtained on samples treated with or without impurities in 1N NaOH for 14 hours at 80°C, together with the parameters for ideal surface. Data for Ca, Sr, Ba were not obtained since the glass surface became rough after this treatment. Data show clearly that some surface layers were formed for Be and Mg while no significant surface layers were formed for plain NaOH, Zn and Al. Surface layer thickness and refractive index were calculated from  $\Delta$  and  $\psi$  and were found to be 1.450 and 620Å for Be and 1.424 and 550Å for Mg respectively, using silica glass refractive index of 1.457. In Figure 3, time dependence of surface layer formation is shown for Ca at 80°C.

Table 1

Ellipsometric parameters on the glass samples treated in 1N NaOH with and without impurity ions at 80°C for 14 hours. Incidence angle is 60°, wave length is 6328Å and refractive index of silica glass is 1.457

	$\Delta$	$\psi$	$n_F$	$d(\text{Å})$
ideal surface	0.00	7.01		
NaOH	0.42	6.99		
Al	-0.06	7.01		
Zn	0.05	6.98		
Be	1.75	7.20	1.450	620
Mg	6.94	7.65	1.424	550
	-0.15	-0.04		

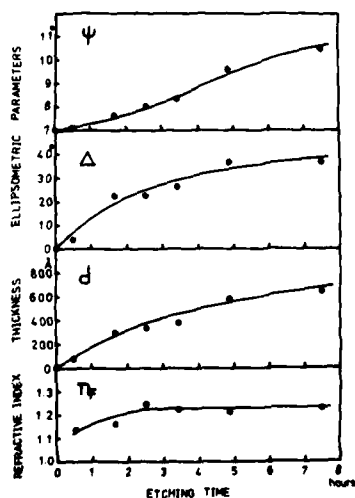


Figure 3.

Ellipsometric parameters ( $\Delta$  and  $\psi$ ), thickness ( $d$ ) and refractive index ( $n_F$ ) of surface layer vs. etching time. The glass was treated in 1N NaOH with 0.001 mol/l.  $\text{CaCl}_2$  at 80°C.

#### 4. X-ray Diffraction Analysis

Figure 4 shows the x-ray diffraction pattern which was obtained on the silica glass sample treated with the calcium-containing solution for 14 hours at 80°C, air dried at RT. The profile shows clearly two peaks indicated by arrows in this figure, together with a broad peak at around  $2\theta \approx 22^\circ$  due to amorphous silica structure. These two peaks can be assigned to the structure of calcium silicate hydrated compound which was identified by Taylor [7] to be C-S-H(1) ( $0.8-1.5 \text{ CaO} \cdot \text{SiO}_2 \cdot 0.5-2.5 \text{ H}_2\text{O}$ ), consistent with our earlier observation [4].

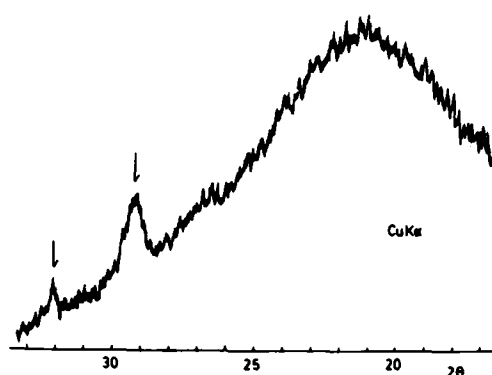


Figure 4.

X-ray diffraction pattern on the glass sample after treatment in 1N NaOH with 0.001 mol/l  $\text{CaCl}_2$  at 80°C for 14 hours.

#### 5. SEM Observation

Figure 5 shows a series of SEM pictures of the silica glass surface after the treatment in alkaline solution containing alkaline earth element for 14 hours at 80°C. Smooth surface was observed for Ba and somewhat rough surface for Mg. For Ca, Sr and Ba, rough and porous surface layers were developed.

#### DISCUSSION

It is clear from the above observation that alkaline earth elements and other elements such as Zn and Al behave differently as corrosion inhibitors. The treatment of glass in NaOH solution with and without Zn, Al addition does not produce the corrosion surface layer. This is clear from the linear time dependency of the etching as well as the ellipsometric parameters which remain, after treatment, essentially the same as those for the ideal glass surface.

On the other hand, the surface corrosion layer was formed when glass was treated with NaOH solution containing alkaline earth elements, as can be seen in SEM picture in Figure 5. For Be, although the surface corrosion layer is not clear from SEM picture only, the ellipsometric parameters in Table I clearly indicate a surface layer. In addition, etching curve in Figure 1 are consistent with surface layer formation; namely, for Ca, Be and Sr-containing solutions, the etching rate

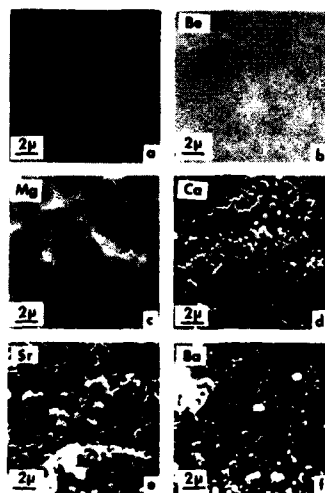


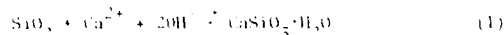
Figure 3.

Scanning electron micrographs of the glass surfaces after treatment in 1N NaOH (a) with 0.001 mol/l  $\text{BeCl}_2$  (b),  $\text{MgCl}_2$  (c),  $\text{CaCl}_2$  (d),  $\text{SrCl}_2$  (e) and  $\text{BaCl}_2$  (f) at  $80^\circ\text{C}$  for 14 hours.

slows down with increasing etching time due to the surface layer formation. Apparently the formed surface layer works as a diffusion barrier. In a longer etching time, a linear time dependence was observed [4] even for calcium containing solution suggesting that a steady state has been reached. For Ba and Mg containing solutions, curves are straight probably because the etching rates of surface layers are so high that the layer formation has practically no effect.

The rate of surface layer formation is continuous with etching time as shown in figure 5 for Ca, where the film thickness increases steadily up to  $700\text{\AA}$  for 8 hours and the refractive index reaches a constant value of 1.22 after 5 hours. The surface layer for Ca was assigned to calcium silicate hydrated compound [7]. Probably similar metal silicate hydrated compounds are formed on silica glass treated with alkaline solution containing other alkaline earth elements. Ellipsometric parameters give somewhat low refractive index, 1.424 for Mg and 1.22 for Ca, while refractive index of C-S-H(1) is 1.494-1.530 [7]. This is because of the porous surface structures as observed in SEM pictures.

The results in Figure 2(a) are considered to result from the metal silicate hydrate formation reaction. Experimental curves can be simulated by calculated ones on the assumption of following simple reactions



And equilibrium constant  $K$  is given by

$$K = \frac{[\text{CaSiO}_3 \cdot \text{H}_2\text{O}]}{[\text{SiO}_2][\text{Ca}^{2+}][\text{OH}^-]^2}$$

Assuming  $[\text{CaSiO}_3 \cdot \text{H}_2\text{O}] = C_0 - C$

$$[\text{Ca}^{2+}] = C$$

$$[\text{SiO}_2] = SW$$

where  $S$  and  $W$  are specific area and weight of porous glass, respectively,

$$K = \frac{C_0 - C}{SWC[\text{OH}^-]^2}$$



and then, for constant  $K$  and  $S$

$$\frac{C}{C_0} = \frac{1}{1 + \alpha w} \quad (2)$$

where  $\alpha$  is proportional to  $[\text{OH}^-]^2$ . Plotting Equation 2 for various  $\alpha$  values, Figure 6 is obtained. The shape of curves in this figure is similar to that in Figure 2(a).

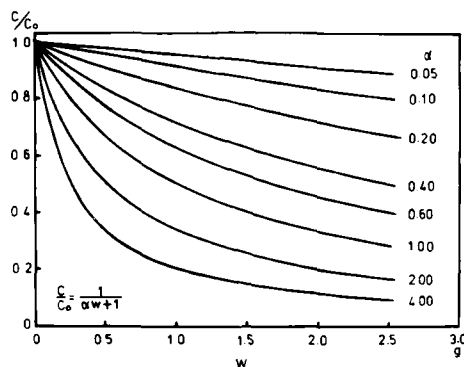


Figure 6.

Calculated  $C/C_0$  vs. weight of porous glass ( $w$ ). See text.

It is clear from the above that the surface corrosion layer is formed in alkaline solution containing alkaline earth element and that this surface layer modifies the subsequent corrosion rate. A similar view was expressed by Ishikawa [8] et al. for the case of alkaline solution containing calcium. It is possible alkaline earth oxide components in glass play the similar role in the alkaline corrosion, since approximately the same order was observed [9] in the corrosion rate of  $\text{MO-SiO}_2\text{-Na}_2\text{O}$  glasses ( $M$  is alkaline earth element).

Another interesting phenomenon observed in this work is crack growth after treatment with Sr and Ba. In Figure 7, the profile of crack growth is shown on the surface of glasses which were treated with Sr or Ba-containing solutions continuously for 14 hours. It is noted that crack growth is enhanced when the sample surface was abraded with 600 grit SiC paper before treatment. It was also found that crack formation is suppressed when the sample was taken out from the solution at an interval of 1 or 2 hours and was washed. Only heavy alkaline earth elements, such as Ba, Sr, exhibit this crack growth. It is most likely that heavy cations are deposited in cracks and extend them to larger size. This crack formation had a drastic effect on the mechanical strength of glass specimens [10].

#### CONCLUSION

An inhibitor effect to reduce the alkaline attack of silica glass was investigated for a series of alkaline earth elements and Zn, Al. Ca and Be were found to be the most effective. A corrosion surface layer was formed on silica glass with the alkaline solution containing alkaline earth element while no surface layer was observed for Zn, Al-containing solution.

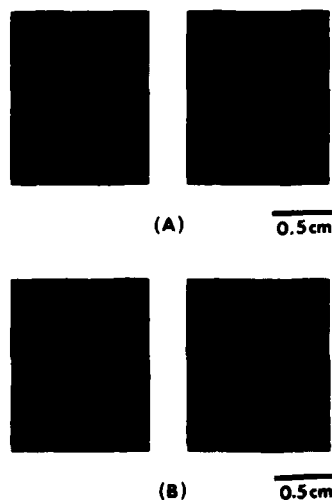


Figure 7.

Glass surfaces after treatment in 1N NaOH with 0.001 mol/l  $\text{SrCl}_2$  (A) and  $\text{BaCl}_2$  (B) at 80°C for 14 hours. Left hand sides are as-received specimen and right hand sides are abraded specimen with 600 grit SiC paper before treatment.

The surface layer, which is a metal silicate hydrated compound, is produced by a reaction between glass surface and impurity alkaline earth ions. This reaction layer works as a corrosion protection film. In the case of the heavy alkaline earth elements such as Sr and Ba, a severe crack formation was observed on the glass surface.

On the other hand, Zn and Al reduce the corrosion rate without forming a surface layer, apparently by a different mechanism.

#### ACKNOWLEDGEMENT

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1. TOS Commercial, Amersil, Inc., N.J.
2. Corning Code 7900(96% $\text{SiO}_2$ ), Corning Glass Works, Corning, N.Y.
3. Rudolph Research, Fairfield, N.J.
4. Advanced Metals Research, Bedford, Mass.

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Appendix II

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Oct 1980

Glass Surface Cracks Caused by Alkaline  
Solution Containing Alkaline Earth Element

by  
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### Abstract

When glass was treated in a hot alkaline solution containing a small amount of heavy alkaline earth elements such as Ba or Sr, sharp cracks formed on the glass surface. The extent of the severity of the crack formation was greater, the heavier the alkaline earth element. The cracks caused a drastic reduction in the mechanical strength of the glass.

Alkaline solution such as NaOH dissolves oxide glasses<sup>1</sup> uniformly, leaving a clear, smooth surface. When the alkaline solution contains a minor concentration of various ions, this dissolution rate is usually retarded.<sup>2,3,4</sup> In the course of the investigation of this inhibitor effect, an unusual phenomenon was discovered. Namely, when certain glasses are held in alkaline solutions containing ions of the heavy alkaline earth elements, Ba or Sr, minute cracks appear on the glass surface. This is shown in Figure 1a, where SiO<sub>2</sub> microscope slide glasses<sup>5</sup> treated in 1N NaOH solution with and without 0.001 mole/l addition of BaCl<sub>2</sub> at 80°C, for 14 hours are compared. When the solution contained no BaCl<sub>2</sub> the glass surface remained clear, while BaCl<sub>2</sub> containing solution produced numerous visible cracks. The size and number of these cracks were observed to increase with the treatment time. Prior abrasion of the specimen promoted the crack formation as can be seen in Figure 1a. A similar phenomenon was observed in Sr containing solution also, although the severity of surface damage was less in Sr containing solution than in Ba containing solution. An example is shown in Figure 1b, where 96% silica glass rods<sup>6</sup> treated in both solutions are compared. No visible crack was formed on glasses treated in alkaline solution containing Be, Mg or Ca. Thus, it appears in general that the surface crack formation tendency is greater, the larger the atomic weight of alkaline earth element in solution.

These minute cracks had, as expected, a drastic effect on the mechanical strength of glass specimens. The mechanical strength was measured using 96% silica glass rods with 3mm diameter, 6.4 cm in length at room temperature and in air (R.H. 50%) using a four point bending method. In figure 2, the mechanical strength, at a constant stress rate of  $1.7 \times 10^2$  MPa/min, of the glass rods treated in 1N NaOH, 1N NaOH + 0.001 mole/l SrCl<sub>2</sub>, or 1N NaOH + 0.001 mole/l BaCl<sub>2</sub> is shown as a function of the treatment time at 80°C. It can be seen from the figure that the drastic decrease in strength occurs in less than 2 hours when the glass is treated with alkaline solution containing Sr or Ba, while no such strength

degradation takes place for glasses treated with 1N NaOH solution. The strength of glasses treated in Ba or Sr containing solution keeps decreasing with time, reaching as low as  $\sim 1/5$  of its strength for the specimen treated in Ba or Sr-free solution in 14 hours. It is known that when alkali metal ions are contained as a glass component, they can exchange with other ions from an external source. This ion-exchange can produce compressive<sup>7</sup> or tensile stresses<sup>8</sup> depending upon the relative size of the exchanging ions. In the present experiment, however, this type of ion-exchange is unlikely since the alkali content in the glass specimens used is extremely low.

Alkaline earth elements were found<sup>4</sup> to deposit on the glass surface and reduce the alkaline attack while other ions such as Zn, Al were not. It is most likely that heavy alkaline earth ions deposit in the pre-existing micro-cracks and cause a crack extension. This phenomenon can be utilized as a means to observe surface flaws.

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### Figure Captions

Figure 1(a) Surface conditions of silica slide glass after immersion in (A) 1N NaOH solution, (B) 1N NaOH + 0.001 mole/l  $\text{BaCl}_2$  solution for 14 hours at 80°C. Sample (C) was abraded with 600 grit SiC paper prior to immersion in the same solution as for (B).

Figure 1(b) Surface conditions of 96% silica glass rod after immersion in (A) 1N NaOH solution, (B) 1N NaOH + 0.001 mole/l  $\text{SrCl}_2$  solution or (C) 1N NaOH + 0.001 mole/l  $\text{BaCl}_2$  solution at 80°C for 14 hours.

Figure 2. Mechanical strength of 96% silica glass rods as a function of the solution treatment time. Each data point represents the average of 30 specimens with  $\pm$  S.D.

●: 1N NaOH solution

■: 1N NaOH + 0.001 mole/l  $\text{SrCl}_2$  solution

▲: 1N NaOH + 0.001 mole/l  $\text{BaCl}_2$  solution

Room temperature, in air. (R.H. 50%)

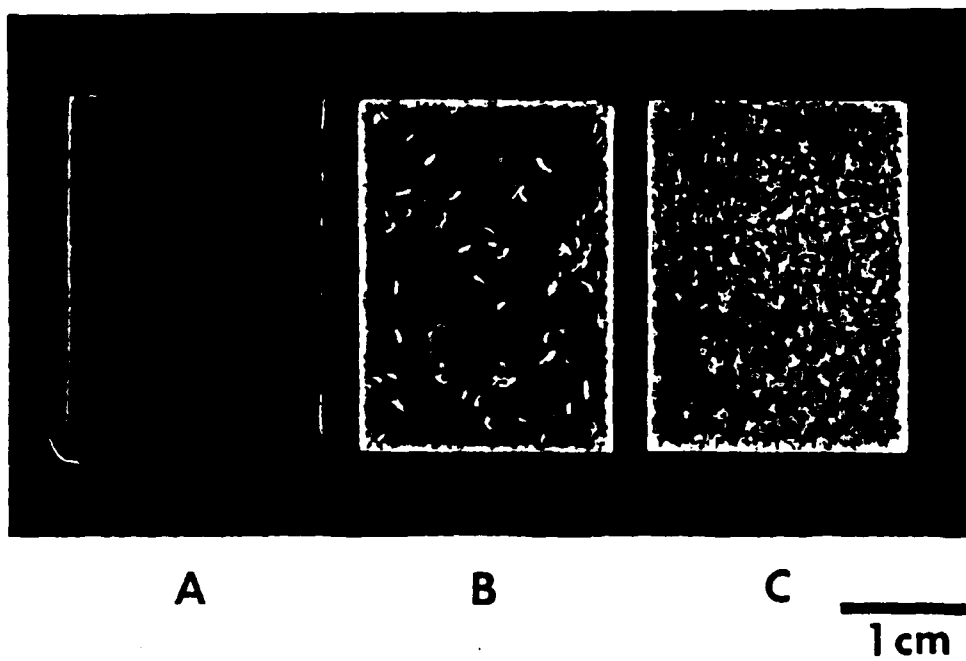
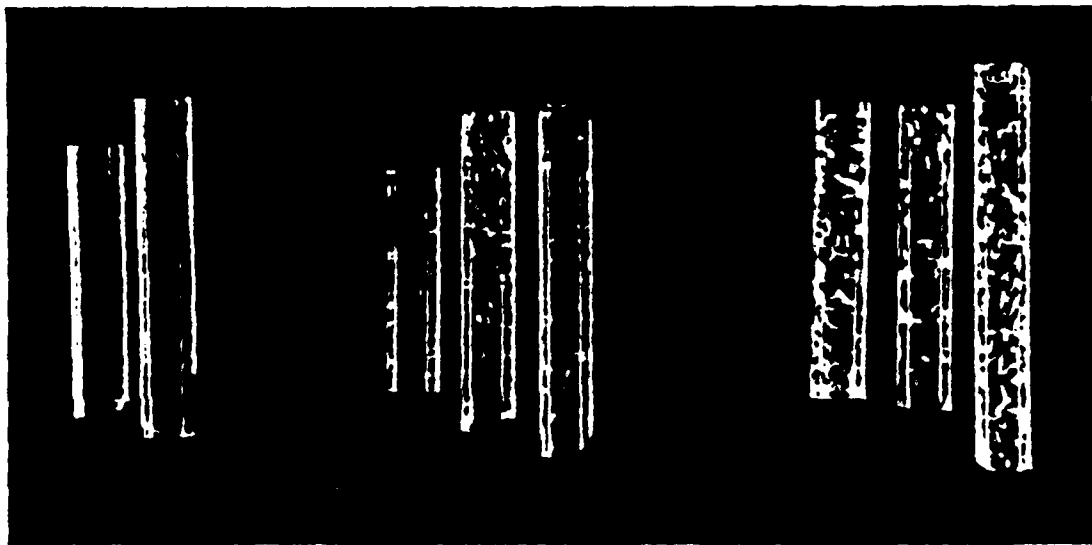


Figure 1(a)



A

B

C

1cm

Figure 1(b)

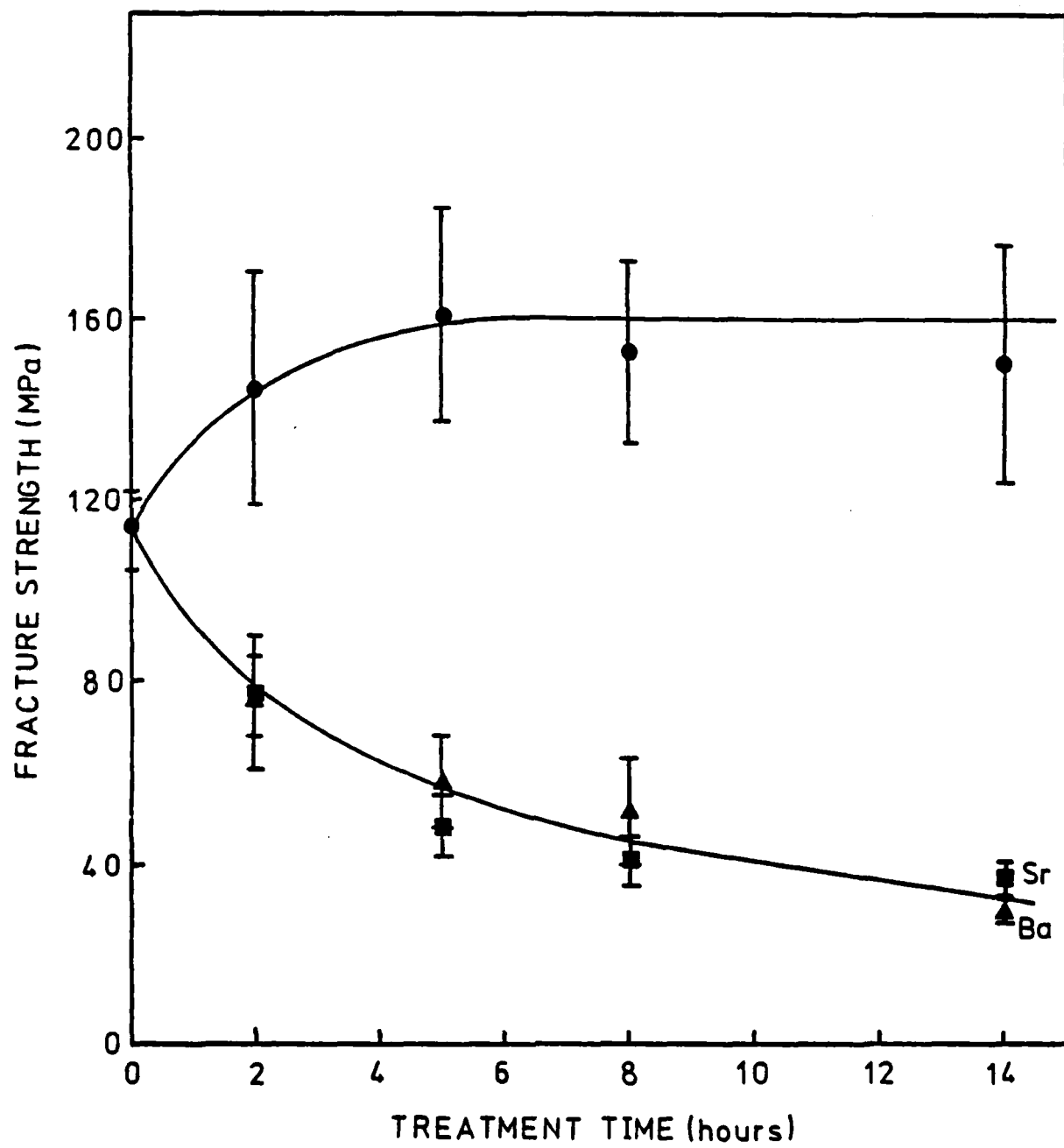


Figure 2

Appendix III

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4. 81

Effect of Surface Energy on the  
Mechanical Strength of a High Silica Glass

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#### ABSTRACT

Mechanical strength of high silica glass was measured in various organic liquids and in water. The extent of the surface energy reduction of glass was also estimated from the swelling, or the expansion of porous glass, immersed in liquids, by measuring the stress in the core of a partially leached glass. The stress, normalized to the value in water, showed a good correlation with the heat of immersion, which is a measure of the surface energy reduction. Mechanical strength and the stress due to swelling showed a reasonable correlation suggesting that the strength variation in various liquids is due to the surface energy variation and the accompanying force which caused the swelling.

## I. Introduction

The mechanical strength of glass is strongly influenced by the environment in which it is measured. For example, the fracture strength measured in water is approximately half of that in vacuum<sup>1,2</sup>. Similar strength reduction was observed in organic solvents<sup>1-5</sup>. There are several suggested mechanisms for the phenomenon. Charles and Hillig explain the phenomenon in terms of chemical attack at the crack tip by water<sup>6</sup>. The reduction in strength in an inert environment, such as organic solvents, could be attributed to the residual water in the organic solvent. To test this mechanism, therefore, organic solvents free of trace amounts of water have to be used. Another mechanism was suggested by Orowan<sup>7</sup>, who attempted to explain the lower strength of glass in water in terms of the lower surface energy. It is known that the surface energy of glass is reduced when the specimen is immersed in water. In order to relate this lowering of the surface energy to the mechanical strength, Orowan used the Griffith equation<sup>8</sup> which expresses the mechanical strength as a function of the surface energy. Subsequently, several investigators<sup>1,5,9</sup> used this mechanism to explain the strength reduction of glass in organic solvents as well as in water vapor. The surface energy in the Griffith equation, however, is the fracture surface energy<sup>8</sup> and although it may be broadly interpreted, as was done by Orowan, to include the effect of the test environment, its relation to the ordinary surface energy which can be evaluated non-destructively<sup>10-12</sup> is not clear. Earlier it was shown<sup>13</sup> by the present authors that the mechanical strength variation in various environments is related to the reduction of the surface energy of glass and the swelling by using a characteristic of liquid, called polarity. Here it will be shown that essentially the same conclusion

can be reached by employing a more popular concept, i.e. heat of immersion<sup>14</sup>, which is a direct measure of the surface energy reduction of a solid immersed in a liquid.

## II. Experimental

### (A) Mechanical Strength Measurement

Vycor brand\* 96% silica glass rods were used in the mechanical strength measurement by four point bending method. The glass rods (3mm in diameter) were cut into approximately 6.4 cm length and dried at 150°C for three hours. The drying temperature of 150°C was chosen since physically adsorbed water is known<sup>15</sup> to be eliminated by heating at this temperature for a short time. The glass surface was abraded by putting 30 glass rods in a 2l jar mill with 70g of 0.3 $\mu$  Al<sub>2</sub>O<sub>3</sub> dry powder in vacuum and tumbling them for 30 minutes. Al<sub>2</sub>O<sub>3</sub> powder was heated in vacuum at 400°C for 6 hrs. to remove water in the powder immediately before placed in the jar mill. Vacuum in the container during drying as well as in the jar mill was less than 10<sup>-2</sup> torr. After abrasion, the glass rods were washed in an ultrasonic cleaner in the same organic solvent as that to be used in the mechanical strength measurement. The fracture strength was measured after immersing a specimen for at least 30 minutes in water or in organic solvents dried by molecular sieves\*\* in advance. Preliminary investigation on the stress rate dependency indicated that, although the mechanical strength of glass varies with the stress rate, its stress rate dependency is similar both in water and in an organic solvent. This suggests that the relative strength in various liquids is independent of stress rate. Consequently all the subsequent measurements were conducted at a constant stress rate of 1.7X10<sup>2</sup> MPa/min.

\* Corning 7900, Corning Glass Works, Corning, New York.

\*\* Linde Molecular Sieves, type 3A, Union Carbide Corp., Morristown, New Jersey



### (B) Surface Energy Measurement by Swelling

There is no accurate, direct method to measure the surface energy of glass rods in liquids. When a glass specimen with large surface area is available, the heat of immersion can be determined, which is a measure of the reduction of the surface energy. Another method is to use the phenomenon of swelling. Namely, when a solid material with large surface area is immersed in a liquid, the volume of the solid specimen increases, and the amount of the volume increase is proportional to the reduction of the surface energy. The volume change can be measured directly. But here, for better accuracy<sup>16</sup>, the extent of swelling, or the volume increase of glass in various liquid environments was determined by measuring the stress built up in a glass layer between two expanding layers. It was anticipated that this phenomenon of swelling can bridge two apparently unrelated effects, namely the surface energy effect and the mechanical effect.

The glass sample used in the swelling study is a borosilicate glass rod\* with the nominal composition of  $\text{SiO}_2$  70,  $\text{B}_2\text{O}_3$  23,  $\text{Na}_2\text{O}$  7 wt%.

The borosilicate glass rod (6mm in diameter) was heat-treated at 550°C for 3 days to induce phase separation. The phase separated rod was cut into a shape of 2.5mm X 3mm cross-section and 100mm length and immersed in 3N HCl saturated with  $\text{NH}_3\text{Cl}$  at room temperature to leach out the alkali borate-rich phase. Leaching was stopped at approximately half way and the partially leached bar was cut into about 3mm in length. The glass piece was rinsed in water and then dried in an oven at 400°C for 5 hours to remove any organic residue. The specimen was immediately placed in water or organic solvent dried with molecular sieves and

\* custom-made glass, Owens-Illinois Technical Center, Toledo, Ohio.

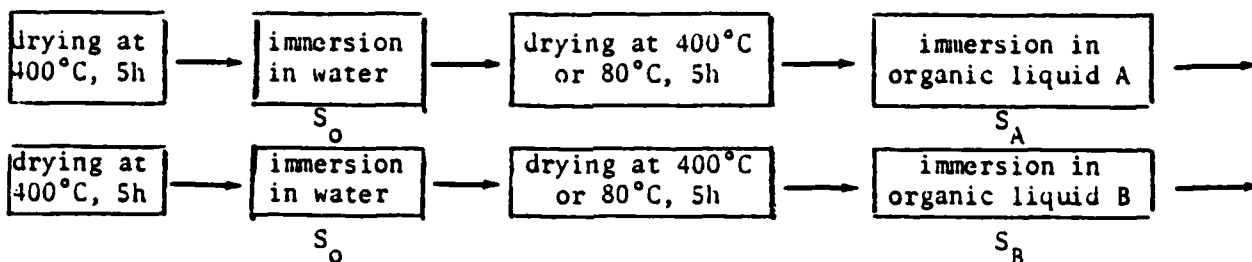
the stress in the center of the unleached core produced by the swelling of the leached clad was measured at room temperature using a polariscope.<sup>\*\*</sup> A micrometer-slide cathetometer with telemicroscope<sup>\*\*\*</sup> was used to observe the birefringence in the specimen placed in the polariscope. The analyzer of the polariscope was rotated with respect to the polarizer and the quarter-wave plate until the minimum light transmission through the specimen is observed, and from the amount of the analyzer rotation the birefringence in the specimen was estimated. The accuracy of the measurement was  $\pm 2^\circ$  in the analyzer rotation angle, which corresponded to  $\pm 2-3$  nm/mm in the present experimental arrangement. The stress in the unleached core rather than in the leached clad was measured to avoid the effect of possible microstructural birefringence of porous glass<sup>17</sup>. Orientation of the specimen with respect to the polarized light path is indicated in Figure 1. Because of the rectangular shaped cross-section, the strains in two perpendicular directions perpendicular to the light path direction are different in magnitude and a birefringence appears. The magnitude of the birefringence is proportional to the stress, which in turn is proportional to the amount of expansion of the clad. Thus, although the absolute magnitude of the stress or the expansion can not be determined by this measurement, the relative magnitude can be determined accurately.

The amount of swelling of the leached layer and the consequent stress generated in the unleached layer are strongly influenced by the surface area and the surface condition of the specimen. Therefore, it is important to use the same specimen with the same surface condition for various liquids in order to

<sup>\*\*</sup> Model No. 204, Polarizing Instrument Co., Inc., Peekskill, New York

<sup>\*\*\*</sup> Gaerther Scientific Corp., Chicago, Illinois

compare the effects of different liquids. To this end the following procedure was employed. The specimen was dried at 400°C for 5 hours for cleaning and then immersed in water for the measurement of stress due to swelling. Subsequently, the specimen was dried at 400°C or 80°C for 5 hours and immersed in each liquid. The birefringence was found to increase with immersion time reaching a steady state value in 12 hours. This steady state value was designated as  $S$ . These values of,  $S$ , in various liquids were normalized to the value in water,  $S_0$ , for the same sample in water after 12 hours. Namely, the process can be expressed as follows:



When the glass used for the swelling experiment is heat-treated for phase separation, and completely leached and subsequently heated for consolidation, it turns into a glass similar to Vycor brand glass<sup>18</sup>, the glass used in the mechanical strength measurement of the present experiment. Thus the phase separated and leached clad has the identical composition as Vycor brand glass. Therefore, the mechanical strength data can be directly compared with the swelling data, since both refer to the same glass composition.

### III. Results

#### (A) Mechanical Strength

The mechanical strength of glass in various liquids is shown in Table 1

in descending order. Here 30 data points were averaged for each liquid, and the error range indicates  $\pm$  standard deviation. It can be seen that the strength varies widely from the highest value of  $(1.48 \pm 0.18) \times 10^2$  MPa in  $\text{CCl}_4$  to the lowest value of  $(1.05 \pm 0.17) \times 10^2$  MPa in water.

#### (B) Surface Energy Measurement by Swelling

When a leached specimen was immersed in liquid, the specimen expanded slowly since a liquid penetrates slowly into the smallest pores, replacing air. Corresponding to the swelling of the leached clad the stress and the birefringence in the unleached core increased with the immersion time reaching a steady state value in approximately 12 hours, as shown in Figure 2 for  $\text{CCl}_4$ . Water was somewhat exceptional and the birefringence kept increasing as shown in the same figure. The birefringence, which is proportional to the stress generated by swelling, expressed by a normalized form  $S/S_0$  obtained after 12 hours immersion in liquid, is shown in Table 2 for both  $400^\circ\text{C}$  and  $80^\circ\text{C}$  drying. The reproducibility was checked by repeated measurement of  $S_0$  and was found satisfactory. The results show that the lowest normalized stress is observed in solvents such as  $\text{CS}_2$ , benzene and  $\text{CCl}_4$ , while the largest stress was generated in water.

#### V. Discussion

Swelling, the volume expansion, of glass can take place by various mechanisms, one of which is the chemical reaction or ion-exchange observed in electrode glass<sup>19</sup>. In the present experiment, alkali content in glass specimens is too low to observe this type of phenomenon. The swelling observed here in the porous glass is related to the surface energy reduction.

Yates<sup>12</sup> showed that the following equation is applicable to the expansion

of the porous glass by gas adsorption.

$$\frac{\Delta l}{l} = \frac{2\epsilon\rho}{9K} \Delta\gamma$$

where  $l$  and  $\Delta l$  are the original length and length change of the specimen, respectively;  $\epsilon$  is the specific surface area;  $K$  is the bulk modulus;  $\Delta\gamma$  is the surface energy reduction, and  $\rho$  is the density of non-porous portion of glass. This expression has been confirmed experimentally<sup>20,21</sup>. In the present experiment, when a porous clad expands by the reduction of the surface energy, a corresponding stress increase in the core was observed. Since the stress in the unleached core which existed before the swelling took place is much smaller than the observed stress,  $S/S_0$  is considered approximately proportional to the reduction of the surface energy. This conclusion can be further confirmed by comparing the stress caused by swelling with the heat of immersion, which is identified with the reduction of the surface energy in liquid. Comparison is made in Figure 3 for a selected liquids. Although the data for heat of immersion for  $\text{SiO}_2$ , (which has a similar composition to the glass used in this investigation), are limited, according to Boyd and Harkins<sup>22</sup> the heat of immersion normalized to that in water,  $^{hi}/(^{hi})_{\text{H}_2\text{O}}$ , depends almost entirely upon the nature of the liquid and not upon the type of oxide immersed. Thus in this figure both values for  $\text{TiO}_2$  and  $\text{SiO}_2$  are used. Figure 3 shows a good correlation between the swelling stress and the heat of immersion, both normalized to values in water. This result indicates that the swelling measured here is a good indication of the surface energy reduction of glass.

The relation between the mechanical strength in various solvents and the

observed  $S/S_0$  values are shown in Figure 4(A) and (B). A reasonable correlation between the strength and  $S/S_0$  is observed with the only exception being nitrobenzene. Nitrobenzene is known to be unique. For example, the lower mechanical strength was observed in this liquid than in water by other investigators<sup>3</sup>. Also, according to Kuznetsov<sup>23</sup>, most liquids show a good correlation between their dielectric constant and the surface energy of glass in the liquid, while nitrobenzene deviates from the trend showing a greater surface energy of glass than expected. (A small amount of acid,  $\text{HNO}_3$  in the solvent may be responsible for the deviation.) Because of the anomaly of this liquid, although the exact reason for this anomaly is not known, the data point for this liquid is shown using a different symbol in Figure 4(A) and (B). With these considerations, it can be seen that there is a reasonable correlation between the mechanical strength and the extent of swelling, which is a measure of the surface energy reduction.

The slight difference between 4(A) and (B) can be attributed to the different surface conditions of the glass produced by different drying temperatures. It is well known<sup>24,25</sup> that the surface hydroxyl concentration decreases with increasing drying temperatures, and that water<sup>15</sup> as well as organic solvents such as benzene<sup>25</sup>, methyl alcohol<sup>26</sup> are adsorbed on the surface hydroxyl. Thus, the number of the surface hydroxyl, and the amount of swelling in a given solvent, of specimen dried at  $400^\circ\text{C}$  are expected to be less than those of specimen dried at  $80^\circ\text{C}$ .

These observations clearly establish that the mechanical strength correlates well with the surface energy reduction. As was pointed out, Orowan's mechanism<sup>7</sup> is not satisfactory since the relation between the surface energy and the fracture surface energy in the Griffith equation is not clearly established. The real

function of the surface energy in the mechanical strength, therefore, is not explicitly included in the Griffith equation. Here, it is suggested that a mechanical force due to the surface energy which produced swelling is responsible for the observed strength variation. Namely, when the surface energy is reduced, the corresponding mechanical force changes producing the swelling of the surface layer. It is speculated that this mechanical force due to the surface energy changes the mechanical strength of glass either directly by changing the local stress and the elastic energy or indirectly by changing the crack tip radius<sup>27</sup>. For example, the surface energy produces a pressure which is proportional to the surface energy and reciprocally proportional to the radius of curvature. Thus this pressure is expected to be large at the crack tip and it works to increase the radius of curvature at the crack tip. When a glass specimen is immersed in water and the surface energy is reduced, this pressure is reduced and the radius of curvature at the crack tip is expected to become smaller. This would lead to the greater stress concentration at the crack tip and the lower mechanical strength in water.

#### Effect of Residual Water

It is important to consider the possible effect of impurity water in various organic solvents on the present observations, since water has the largest effect both on mechanical strength and swelling of glasses. In the present experiment reagent grade chemicals were used and all liquids were treated with molecular sieve. The specified concentrations of water in these organic solvents before the treatment with the molecular sieve are shown, together with the solubility<sup>28</sup> of water in selected organic solvents in Table 3. It has been claimed<sup>29</sup> that after molecular sieve treatment the water content is reduced to <10 ppm in most cases and to <1 ppm in some cases.

When a dried glass is placed in such solvents, water will be adsorbed on the glass surface selectively<sup>30-32</sup>. The fugacity,  $f$ , of water in a solvent with extremely low concentration,  $X$ , of water is given<sup>30</sup> approximately by

$$f = P_o \cdot \frac{X}{X^S}$$

where  $P_o$  is the saturation vapor pressure of the pure water, and  $X^S$  is the solubility of water in the solvent. If we take benzene containing 1 ppm of water at 25°C as an example of solvent,

$$f = 23.8 \text{ mmHg} \cdot \frac{10^{-6}}{0.06 \times 10^{-2}} = 0.0398 \text{ mmHg}$$

It is possible, using this fugacity value, to estimate the extent of the selective water adsorption from the solvent, on the glass surface<sup>31,32</sup>. The maximum amount of water adsorption can be obtained by assuming that the solvent is not adsorbed and using the adsorption data of pure water vapor with the same vapor pressure<sup>31</sup>.

From the adsorption isotherm, the reduction,  $\pi$ , of the surface energy of the solid can be calculated<sup>11</sup>, using the following equation.

$$\pi = \frac{RT}{VE} \int_0^P \frac{V}{P} dP$$

where  $R$  is the gas constant,  $T$  the absolute temperature,  $V$  the molar volume of gas;  $E$  the specific surface area of the solid,  $P$  the equilibrium pressure of the adsorbed gas and  $v$  the volume of gas adsorbed per gram of solid. Using this relation, Boyd and Livingston<sup>33</sup> estimated the surface energy reduction of  $\text{SiO}_2$  upon immersion in saturated vapor at 25°C, and obtained  $244 \times 10^{-7} \text{ J/cm}^2$  for water and  $52 \times 10^{-7} \text{ J/cm}^2$  for benzene. The reduction in the surface energy of the specimen



immersed in the corresponding liquids is expected to be larger. It is possible to obtain the reduction in the surface energy of solid as a function of vapor pressure using the same equation.

When porous high silica glass is immersed in benzene containing 1 ppm of water, the reduction in the surface energy of the solid is estimated, by assuming that benzene is not adsorbed on the glass surface, to be less than 1.5% of the surface energy reduction in the saturated water vapor<sup>34</sup>. If the values obtained by Boyd and Livingston<sup>33</sup> are used here, the reduction of the surface energy reduction due to 1 ppm impurity water in benzene is less than  $3.7 \times 10^{-7} \text{ J/cm}^2$ , far smaller than the surface energy reduction by pure benzene,  $52 \times 10^{-7} \text{ J/cm}^2$ . This difference is actually even greater since the amount of water adsorption from benzene containing 1 ppm water is less while the surface energy reduction by pure benzene liquid is larger than the above value obtained for the saturated benzene vapor. Thus, the effect of trace amount of water can be neglected here.

It is known that a small amount of water vapor in air or  $\text{N}_2$  gas<sup>35</sup> can influence the mechanical strength and the similar effect may be expected for the measurement in organic solvents. From the above discussion, however, it is clear that there is a subtle difference, as far as the effect of small amount of water is concerned, between the measurement in air (or  $\text{N}_2$  gas) and that in organic solvents<sup>36</sup>. In the case of the measurement in air (or  $\text{N}_2$  gas) at room temperature, only water vapor can be adsorbed and other species such as  $\text{O}_2$ ,  $\text{N}_2$  can hardly be adsorbed. Therefore, a small amount of water vapor can have the damaging effect on the mechanical strength. On the other hand, in the measurement in organic solvent, in addition to the selective adsorption of impurity water on the glass surface, the solvent itself, which is the major component, such as benzene, can

also be adsorbed. And, as long as the effect of the adsorbed organic solvent outweighs the effect of the adsorbed water, the effect of water on the measurement can be neglected.

#### CONCLUSION

A correlation was found between the mechanical strength of a high silica glass in various liquids and the extent of swelling or the expansion of the specimen determined by the stress measurement in the unleached core of the partially leached porous borosilicate glass. The swelling is a measure of the reduction of the surface energy. It was suggested, therefore, that the strength variation of glass in liquid can be explained by the change in mechanical force due to the surface energy, which caused the swelling.

#### ACKNOWLEDGEMENT

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## Figure Captions

- Figure 1. Partially leached glass specimen and the polarized light path for the stress measurement by a polariscope.
- Figure 2. Immersion time dependence of birefringence in the unleached core in water and  $\text{CCl}_4$ . The birefringence is expressed by the optical retardation. The specimen was dried at  $400^\circ\text{C}$  for 5 hours prior to immersion.
- Figure 3. The relation between the stress in a core of a partially leached glass immersed in various liquids normalized to the value in water vs. the normalized heat of immersion. •  $\text{TiO}_2$ ,  $\text{SiO}_2$  (ref. 20).
- Figure 4. Fracture strength of high silica glass rods vs. normalized swelling stress,  $(S/S_0)$  in various organic solvents. The stress rate was  $1.7 \times 10^{-2} \text{ MPa/min}$ . (A) Specimen dried at  $400^\circ\text{C}$  for 5 hours prior to the swelling stress measurement in organic solvents. (B) Specimen dried at  $80^\circ\text{C}$  for 5 hours prior to the swelling stress measurement in organic solvents.

Table 1

Fracture strength of Vycor brand high silica glass rods\* in various organic solvents at the stress rate of  $1.7 \times 10^{-2}$  MPa/min.

Liquid	Fracture Strength ( $10^2$ MPa)
$\text{CCl}_4$	$1.43 \pm 0.18$
Aniline	$1.37 \pm 0.19$
Benzene	$1.36 \pm 0.13$
$\text{ClCl}_3$	$1.28 \pm 0.12$
Ethanol	$1.28 \pm 0.19$
Formamide	$1.23 \pm 0.10$
Nitrobenzene	$1.14 \pm 0.14$
Methanol	$1.07 \pm 0.12$
Water	$1.05 \pm 0.17$

\* Corning 7900, Corning Glass Works, Corning, N.Y.

Table 2

Normalized swelling stress values in various organic solvents.  $S$  and  $S_0$  are the stress in the unleached core in an organic solvent and water, respectively.

Liquids	$S/S_0$	$S/S_0$
	dried at 400°C for 5 hours prior to immersion in organic solvents	dried at 80°C for 5 hours prior to immersion in organic solvents
CS <sub>2</sub>	0.22 ± 0.01	0.52 ± 0.02
Benzene	0.22 ± 0.02	0.57 ± 0.03
CCl <sub>4</sub>	0.23 ± 0.03	0.55 ± 0.03
Toluene	0.23 ± 0.02	0.55 ± 0.02
Nitrobenzene	0.24 ± 0.02	0.60 ± 0.05
Chlorobenzene	0.24 ± 0.04	0.57 ± 0.02
CHCl <sub>3</sub>	0.25 ± 0.02	0.65 ± 0.06
Aniline	0.30 ± 0.03	0.62 ± 0.05
Pyridine	0.31 ± 0.01	0.71 ± 0.03
Ethanol	0.37 ± 0.02	0.71 ± 0.02
Propanol	0.42 ± 0.02	0.70 ± 0.03
Formamide	0.49 ± 0.02	0.75 ± 0.03
Methanol	0.51 ± 0.02	0.87 ± 0.03

Table 3

Solubility and specified content of water in selected organic solvents before  
molecular sieve treatment

<u>Liquids</u>	<u>Specified Conc. (wt%)</u>	<u>Solubility at 25°C (wt%)</u>
$\text{CCl}_4$	0.01	0.01
$\text{CS}_2$	< 0.05	0.01
Toluene	0.01	0.05
Benzene	0.05	0.06
Chlorobenzene	0.02	0.04
$\text{CHCl}_3$	(0.75 $\text{C}_2\text{H}_5\text{OH}$ )	0.08
Pyridine	0.05	---
Nitrobenzene	(0.003 $\text{HNO}_3$ )	---
Aniline	---	---
Propanol	---	---
Ethanol	(Anhydrous)	---
Methanol	0.05	---
Formamide	---	---

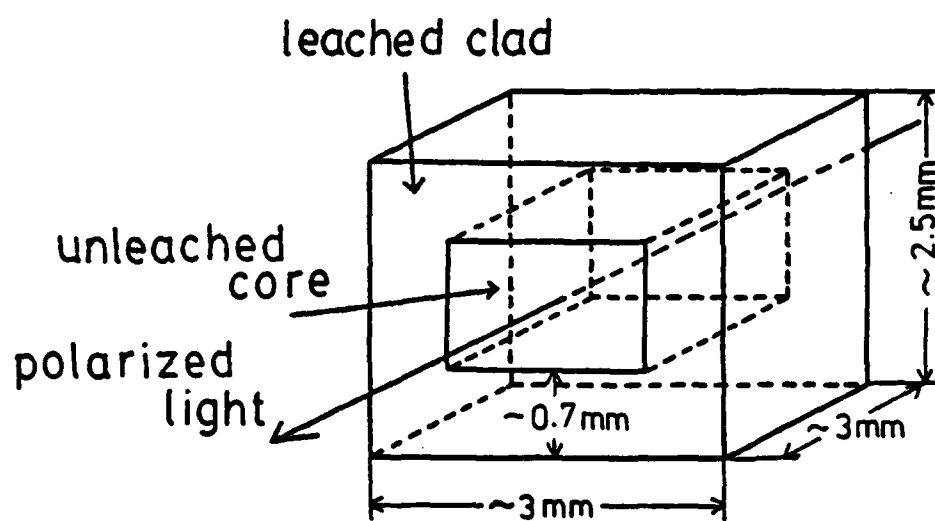
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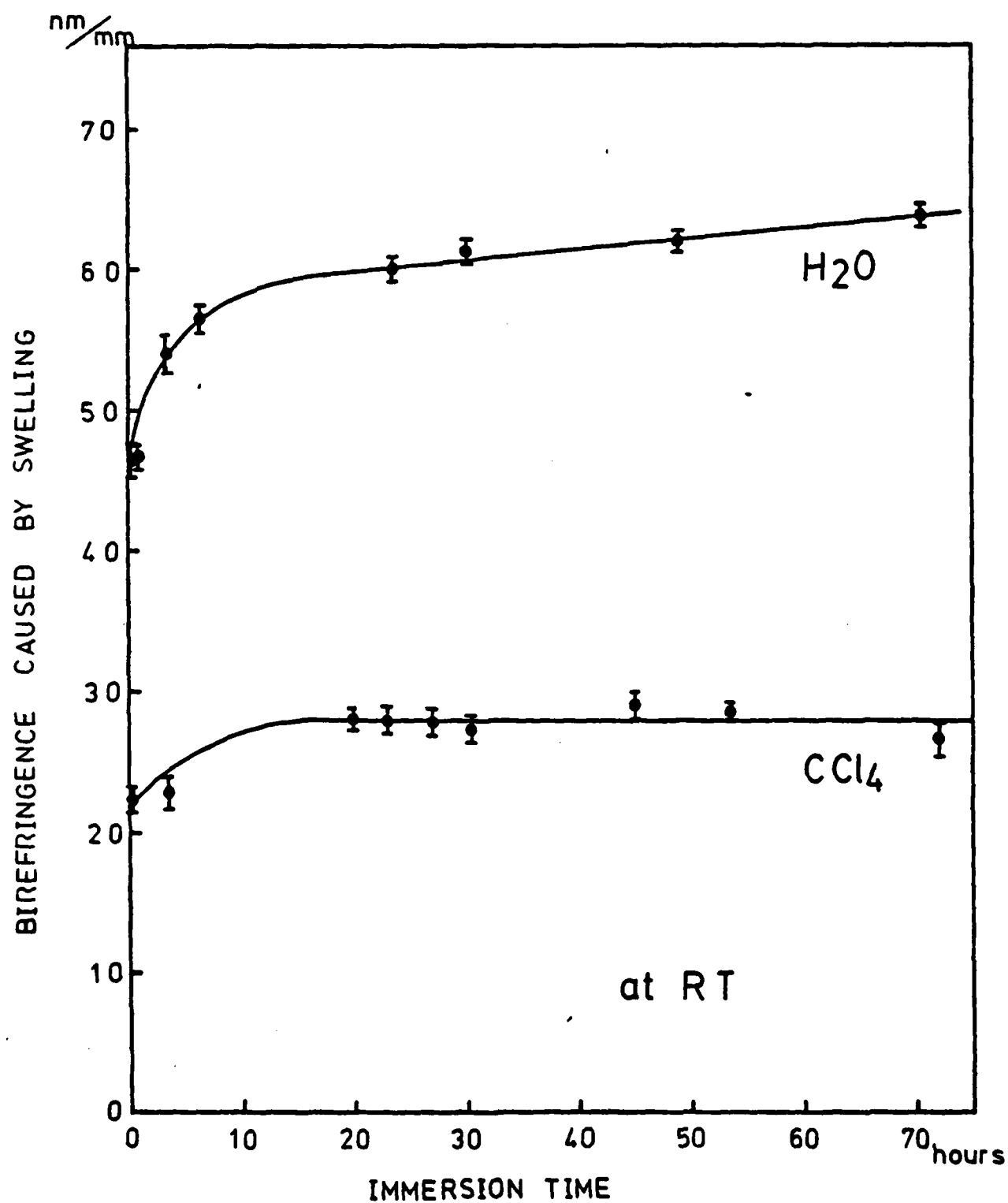
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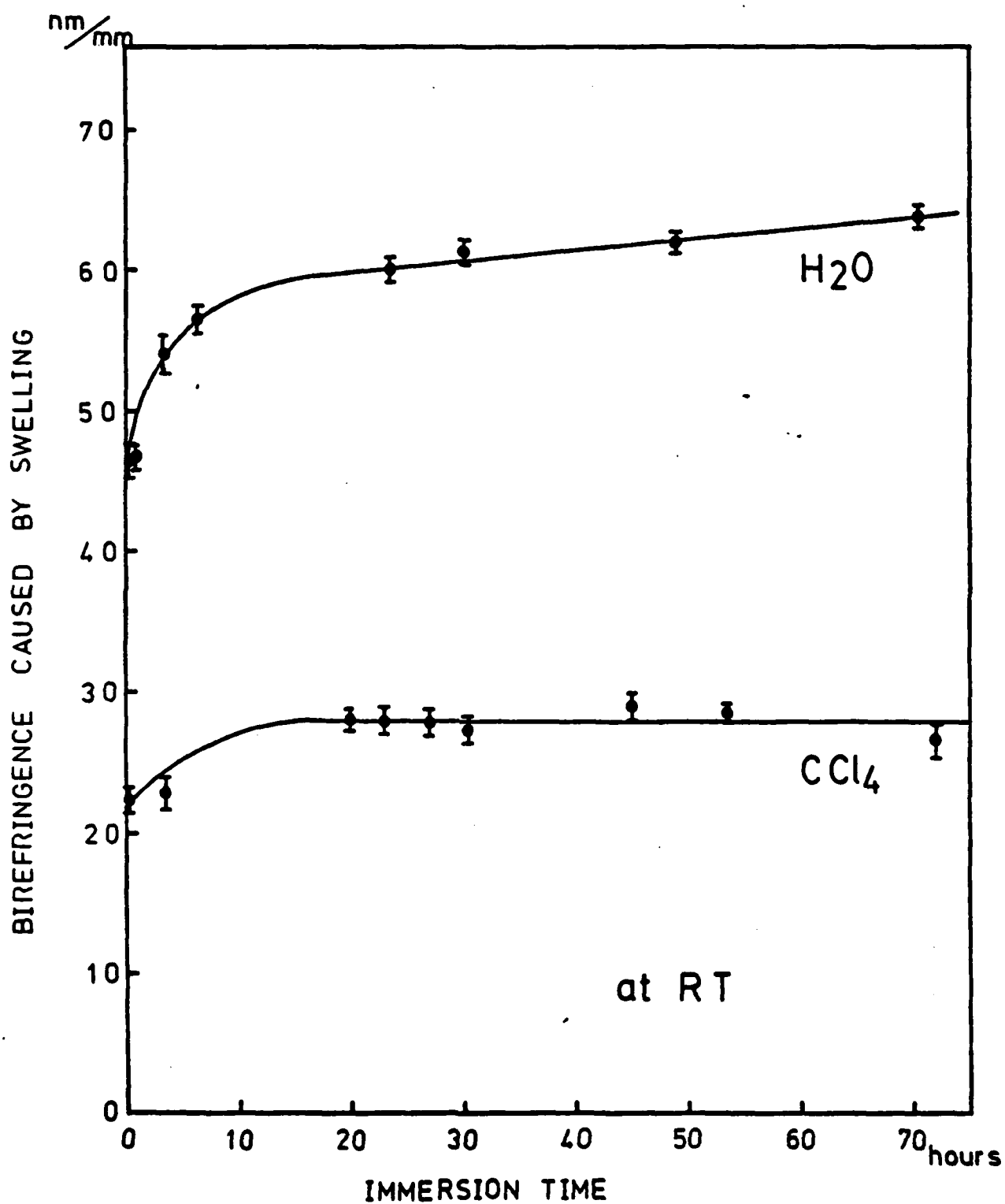
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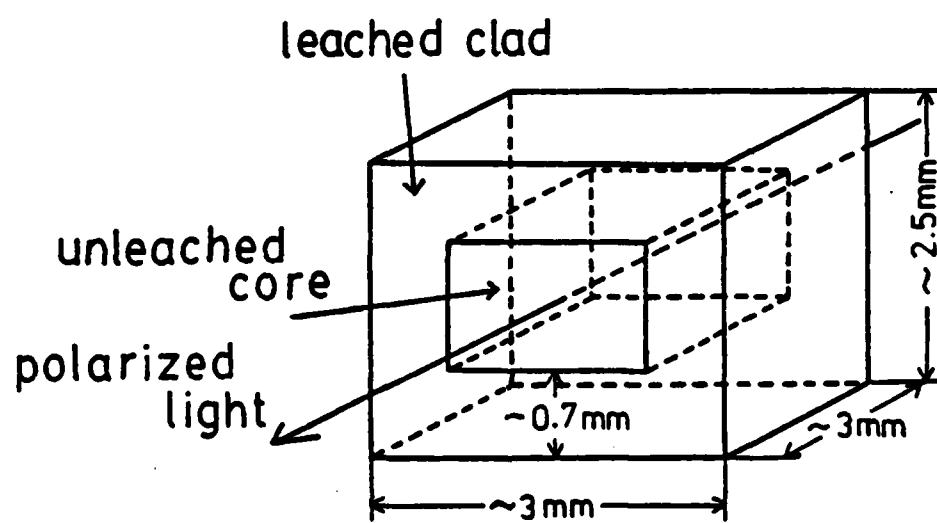


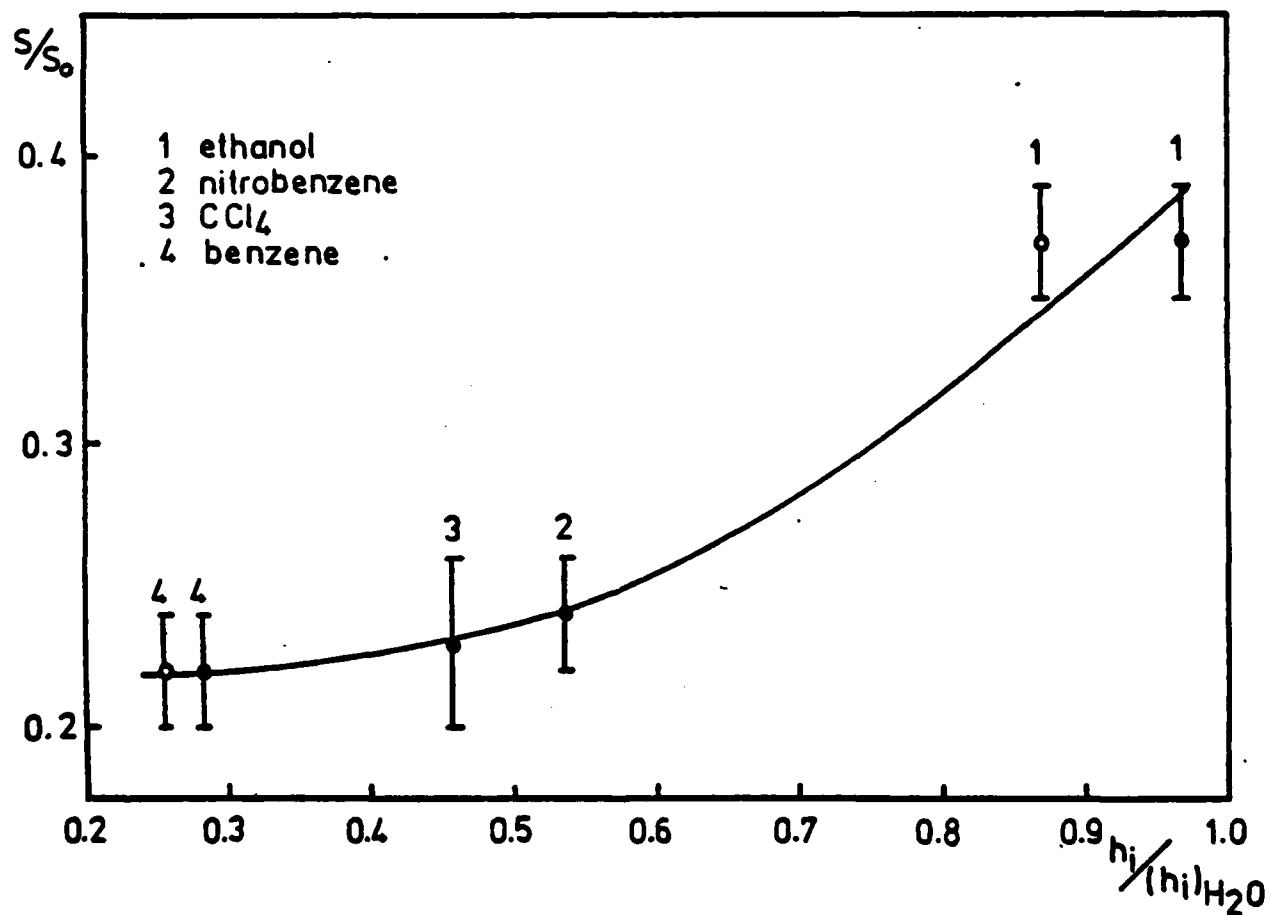
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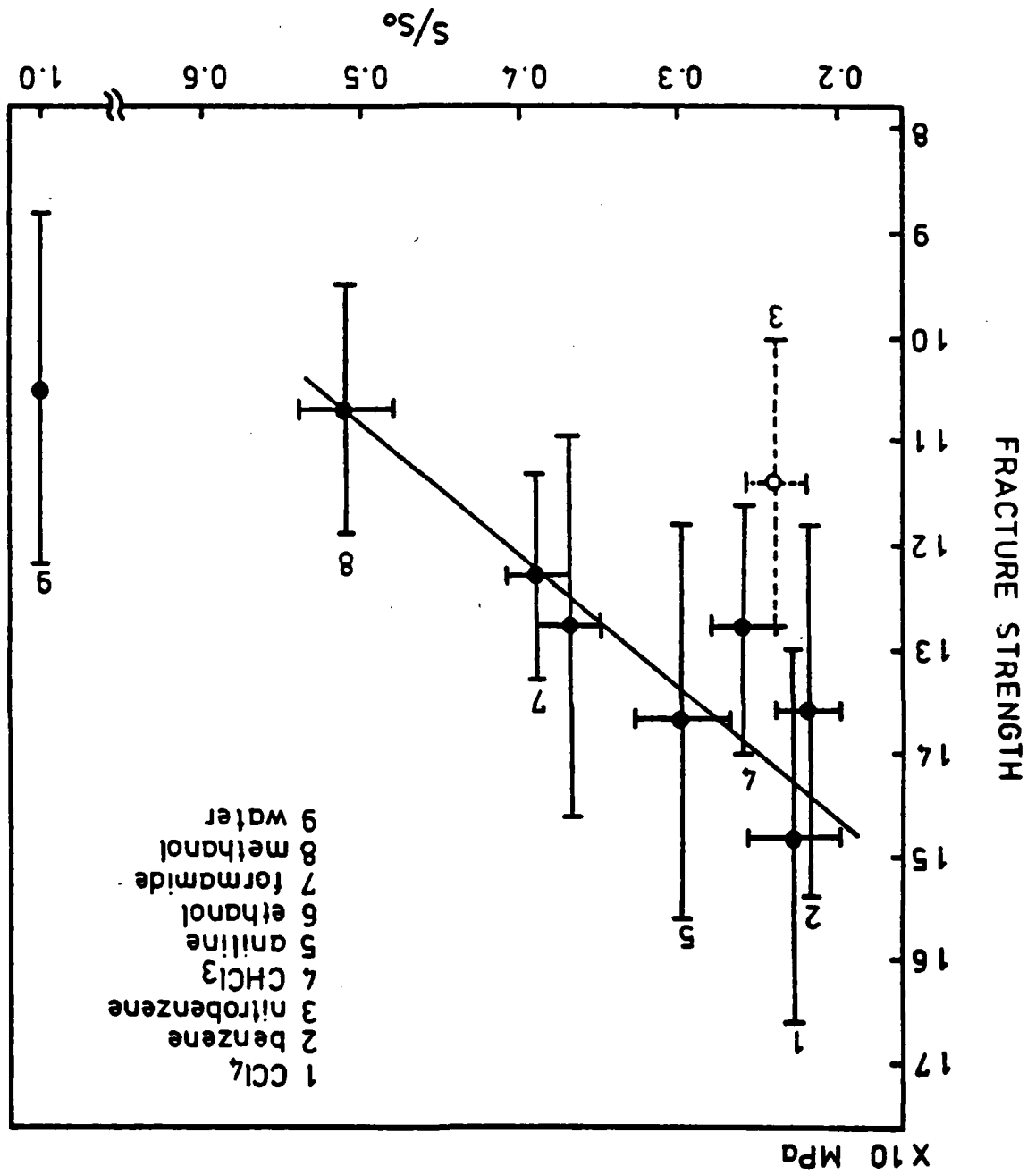


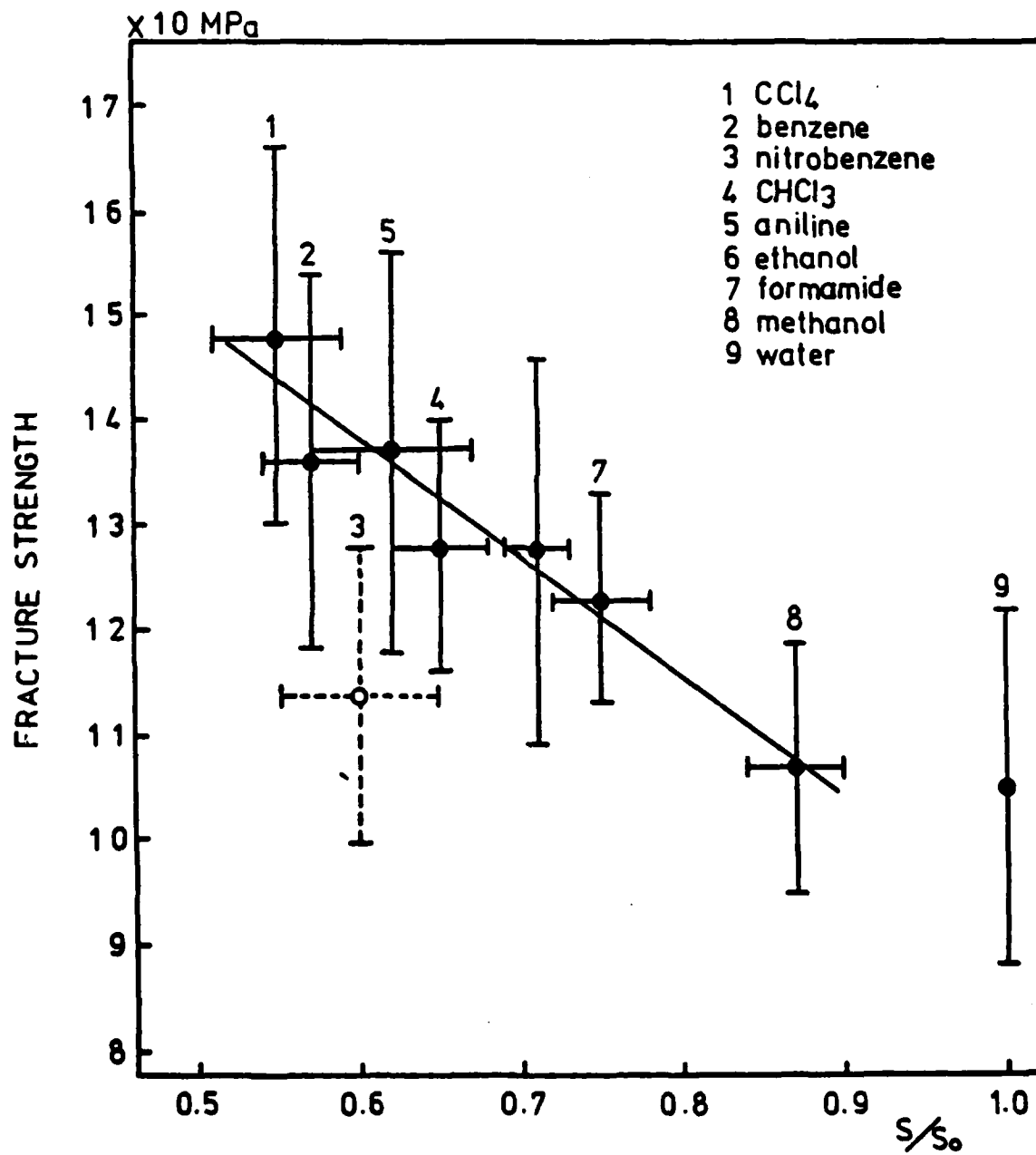














## Appendix IV

### ENVIRONMENTAL EFFECT ON THE MECHANICAL STRENGTH OF GLASS

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#### INTRODUCTION

It is well known that the mechanical strength of glass is strongly influenced by the environment in which it is measured. For example, the strength measured in water is much lower than that in vacuum.<sup>1,2</sup> A similar strength reduction is observed, to a lesser extent, in various organic solvents.<sup>1-5</sup> The strength reduction of glass in water is usually explained by the stress corrosion mechanism by Charles and Hillig.<sup>6</sup> It is difficult, however, to invoke this stress corrosion mechanism for the effect in organic solvents which do not react with glasses.

Alternative explanation was offered earlier by Orowan<sup>7</sup> who believes that the surface energy term  $\gamma$  in the Griffith equation,<sup>8</sup>

$$\sigma_f = \sqrt{\frac{2\gamma E}{\pi C}}$$

is modified by solvent. In this equation,  $\sigma_f$  is the fracture strength,  $E$  is the Young's modulus, and  $C$  is the half length of a thin crack. However, the surface energy in the Griffith equation is related to the energy needed to create a new surface by fracture (fracture surface energy) and is a unique characteristic of material. This fracture surface energy should not be confused, therefore, with the surface energy which is influenced by the environment.

The phenomenon of strength reduction of glass in solvent appears similar to liquid metal embrittlement and a similar mechanism may be operating. As a possible mechanism of liquid metal embrittlement, the reduction of cohesive force<sup>9,10</sup> by adsorption has been

## THEORY

Surface energy under consideration will be designated as  $\gamma_s$ , to distinguish it from the fracture surface energy  $\gamma_f$ , used in the Griffith equation. In a solid material, what is related to the mechanical behavior such as contraction of a small particle or swelling of a material with large surface area is the surface stress  $\sigma_s$  which is related to the surface energy by the following relation in the case of isotropic material<sup>17</sup>

$$\sigma_s = \gamma_s + \frac{d\gamma_s}{d\epsilon_s} \quad (1)$$

where  $\epsilon_s$  is the surface strain.  $\gamma_s$  is positive but  $\frac{d\gamma_s}{d\epsilon_s}$  can be either positive or negative. The latter is zero for liquid. Therefore, for a solid, in general,  $\sigma_s$  is an unknown quantity, which can be positive or negative. But experimental observations of the reduced lattice constants in small particle as well as swelling, volume expansion by the reduction of the surface energy indicate that  $\sigma_s$  is a positive quantity. Furthermore,  $\frac{d\gamma_s}{d\epsilon_s}$  appears to be a constant for a given material, independent of  $\epsilon_s$  for small  $\epsilon_s$ , judging from the lattice constant dependency on particle size of gold.<sup>15</sup> Then, when  $\gamma_s$  is changed for example by adsorption, the change in the surface energy can be equated to the change in the surface stress, namely

$$\Delta\sigma_s = \Delta\gamma_s \quad (1)'$$

In addition to the surface stress described above there is an extra pressure due to the curved surface. This pressure  $P$  is given in general by

$$P = \sigma_s \left( \frac{1}{r_1} + \frac{1}{r_2} \right) \quad (2)$$

where  $r_1$ ,  $r_2$  are principal radii of curvature.

When a crack in a thin plate is considered, the pressure is directed inward and its magnitude is given by

$$P = \frac{\sigma_s}{r} \quad (2)'$$

where  $r$  is the radius of the curvature of crack, which, in general, is a function of position. The magnitude and position dependence of the pressure vary with the crack geometry. When an elliptic crack with the form

$$\frac{x^2}{a^2} + \frac{y^2}{b^2} = 1 \quad (3)$$

is assumed,  $r$  is given by

$$r = \frac{(b^4 x^2 + a^4 y^2)^{3/2}}{a^4 b^4} \quad (4)$$

which has the minimum value, at  $x=a$ ,  $y=0$ , of

$$r_{\min} = \rho = \frac{b^2}{a} \quad (5)$$

Two examples of the position dependence of normalized pressure for elliptic crack are shown in Figure 1. Although exact geometry of crack is not known, crack length  $C=a\sqrt{6}$  and the crack tip radius of  $\rho \sim 20\text{\AA}$  have been suggested for glass.<sup>18</sup> The examples in Figure 1 correspond approximately to these values. On the other hand if the crack tip appears like a part of the circle, the pressure due to the surface energy in this portion should be constant.

There are two principal methods to derive expressions for the mechanical strength of a brittle material. One is to equate the local stress at a crack tip derived by Inglis<sup>19</sup> to the theoretical strength of the material and the other is to consider the energy balance at the time of fracture, first performed by Griffith.<sup>8</sup> Both methods are known to give similar expressions. Here effects of surface energy on these two derivations will be considered. In addition, the effect of surface energy on the crack geometry variation and the consequent mechanical strength variation will be considered.

### Stress Balance

According to Inglis,<sup>19</sup> the stress  $\sigma_c$  at the tip of a thin crack subjected to the external stress  $\sigma$  in perpendicular direction to the crack length is given by

$$\sigma_c = 2\sigma\sqrt{\frac{C}{\rho}} \quad (6)$$

where  $\rho$  is the radius of curvature at the crack tip. Equating this to the theoretical strength of glass  $\sigma_{th}$  given by

$$\sigma_{th} = \sqrt{\frac{E\gamma_f}{a_0}} \quad (7)$$

where  $a_0$  is the interatomic spacing, the expression for the fracture strength of glass is given by

$$\sigma_f = \frac{1}{2} \sqrt{\frac{E\gamma_f}{a_0} \frac{\rho}{C}} \quad (8)$$

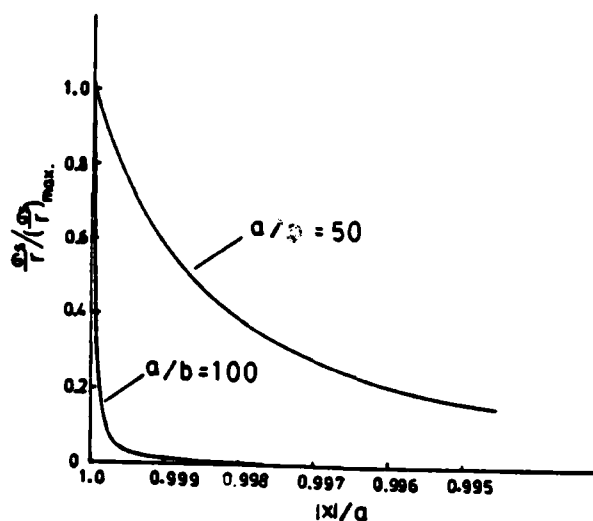


Fig. 1. Normalized pressure by the surface stress vs. normalized distance from crack tip for elliptic crack with two different axis ratios.

The presence of the extra pressure due to the surface energy will modify this expression. For simplicity, if this pressure  $P$  is assumed constant, as would be approximately the case if the crack tip had the shape of a part of a circle, the tangential stress at the crack tip due to this pressure is given by<sup>20</sup>

$$-2P \sqrt{\frac{C}{\rho}}$$

Adding this to the stress due to the applied stress, the stress at the crack tip will become

$$\sigma_c = 2\sigma \sqrt{\frac{C}{\rho}} - 2P \sqrt{\frac{C}{\rho}} \quad (9)$$

Equating this to the theoretical strength  $\sigma_{th}$

$$\sigma_f = \frac{1}{2} \sqrt{\frac{E\gamma_f}{a_0}} \frac{\rho}{C} + P \quad (10)$$

is obtained, where  $P = \frac{\sigma_s}{r}$ .

This result indicates that the strength increases with the surface stress (or energy) and that the effect is greater, the smaller the radius of curvature at the crack tip portion.

### Energy Balance

The energy change  $E_T$  associated with a thin crack formation is given by Griffith<sup>8</sup> as

$$E_T = -\frac{\pi C^2 \sigma^2}{E} + 4C\gamma_f \quad (11)$$

where the first term of the right hand side is the strain energy and the second term is due to the fracture surface energy. The strength expression

$$\sigma_f = \sqrt{\frac{2E\gamma_f}{\pi C}} \quad (12)$$

is obtained from equation (11) by setting  $\frac{\partial E_T}{\partial C} = 0$ . In this derivation of the Griffith equation, the effect of the surface energy of the existing crack surface has not been considered. The extra stress by the surface energy tends to operate in the opposite direction to the external stress and to reduce the magnitude of the strain energy. If, for simplicity, the stress due to the surface energy  $\sigma_s$  is assumed constant, independent of position, then its contribution to the strain energy can be calculated<sup>20,21</sup> and the energy change associated with a crack becomes

$$E_T = -\frac{\pi C^2 \sigma^2}{E} + \frac{\pi C^2 P^2}{E} + 4C\gamma_f \quad (13)$$

The critical stress is obtained by setting the derivative of the equation (13) zero. Then,

$$\sigma_f = \sqrt{\frac{2\gamma_f E}{\pi C} + P^2} \quad (14)$$

An additional energy change can result from the deformation of the crack tip by the applied stress and the consequent change in the surface area. Again considering an elliptic hole in a thin plate with unit thickness, the increase in the surface area by a biaxial tensile stress can be calculated.<sup>20</sup> The original surface area,  $l$ , of the elliptic crack is

$$l = 4a \int_0^{\pi/2} \sqrt{1 - K \sin^2 \phi} d\phi \quad (15)$$

where

$$K = \frac{\sqrt{a^2 - b^2}}{a} \quad (16)$$

This changes, by external stress  $\sigma$ , to

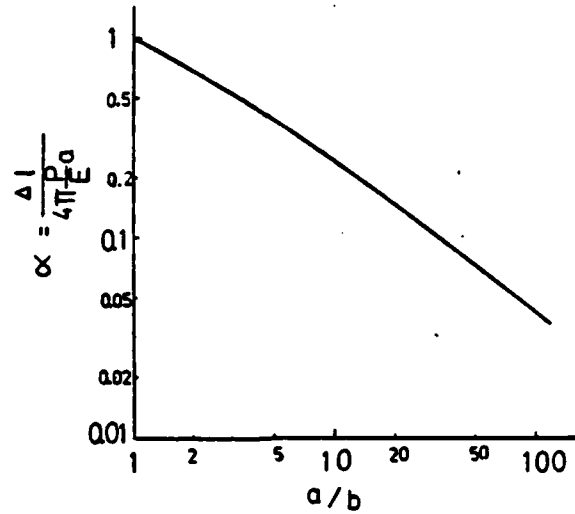


Fig. 2 A parameter of surface area variation of elliptic crack vs. axis ratio.

$$l + \Delta l = 4a \int_0^{\pi/2} (1 + \epsilon_\theta) \sqrt{1 - K^2 \sin^2 \phi} d\phi \quad (17)$$

where  $\epsilon_\theta$  is the tangential strain on the crack surface given by

$$\epsilon_\theta = \frac{2\sigma}{E} \frac{ab}{a^2 \sin^2 \theta + b^2 \cos^2 \theta} ; \cos \theta = \frac{x}{a} \quad (18)$$

These integrals are tabulated and the increase in the surface area can be expressed as

$$\Delta l = \alpha \cdot 4\pi a \frac{P}{E} \quad (19)$$

where  $\alpha$  depends upon the shape of the crack and is shown in Figure 2. Thus, the total energy change is given by using  $a = c$

$$E_T = -\frac{\pi C^2 \sigma^2}{E} + \frac{\pi C^2 P^2}{E} + \alpha \cdot 4\pi C \frac{\sigma}{E} \sigma_s + 4C\gamma_f \quad (20)$$

Proceeding in a similar fashion as before

$$\begin{aligned} \frac{\partial E_T}{\partial C} &= -\frac{2\pi C \sigma^2}{E} + \frac{2\pi C P^2}{E} + \alpha \cdot 4\pi \frac{\sigma}{E} \sigma_s + 4\gamma_f = 0 \\ \therefore \sigma_f &= \alpha \frac{\sigma_s}{C} + \sqrt{\alpha^2 \frac{\sigma_s^2}{C^2} + P^2 + \frac{2\gamma_f E}{\pi C}} \quad (21) \end{aligned}$$

For a circular shaped crack with radius  $r$ ,  $P$  is a constant given by  $\sigma_s/r$ . In the case of an elliptical crack,  $P$  is not a constant, and varies with the position of the crack, as shown in Figure 1, but it remains to be proportional to  $\sigma_s$ . In general, therefore, in the equations (10), (14) and (21),  $P$  should be replaced by  $f\sigma_s$ , where  $f$  is a constant determined by the geometry of crack.

#### Modification of the Crack Geometry

In addition to the effects considered above, the excess pressure by the surface energy can modify the crack tip geometry. When a circular hole with radius  $r$  in a plate is subjected to a uniform inward pressure,  $P$ , the uniform radial displacement  $v_r$  is obtained,<sup>20</sup>

$$v_r = -\frac{P(1+\nu)}{2E} r \quad (22)$$

where  $\nu$  is the Poisson's ratio and  $E$  is the Young's modulus.

Assuming the same magnitude of deformation takes places at the crack tip by the pressure of the type shown in Figure 1, and using the typical value of  $E = 7 \times 10^{11}$  dyne/cm<sup>2</sup>,  $\nu = 0.22$  for glasses, the maximum strain at the crack tip was estimated and shown in Table 1. These values suggest that an appreciable deformation of crack tip takes place. The schematic diagram of this crack tip deformation is shown in Figure 3 for the case of an elliptic crack with  $\frac{a}{b} = 100$ . It is expected that the radius of curvature at the crack tip  $\rho$  becomes larger with increasing surface stress and that the mechanical strength becomes higher correspondingly by the equation (8).

Table 1

9

Estimated Maximum Strain at the Crack Tip, Assuming Equation (22)  
For Various Surface Energy and Crack Tip Radius.

	Strain
$\gamma = 1000 \text{erg/cm}^2$ $\rho = 2 \text{\AA}$	8.7%
$\gamma = 1000 \text{erg/cm}^2$ $\rho = 20 \text{\AA}$	0.9%
$\gamma = 300 \text{erg/cm}^2$ $\rho = 2 \text{\AA}$	2.6%
$\gamma = 300 \text{erg/cm}^2$ $\rho = 20 \text{\AA}$	0.3%

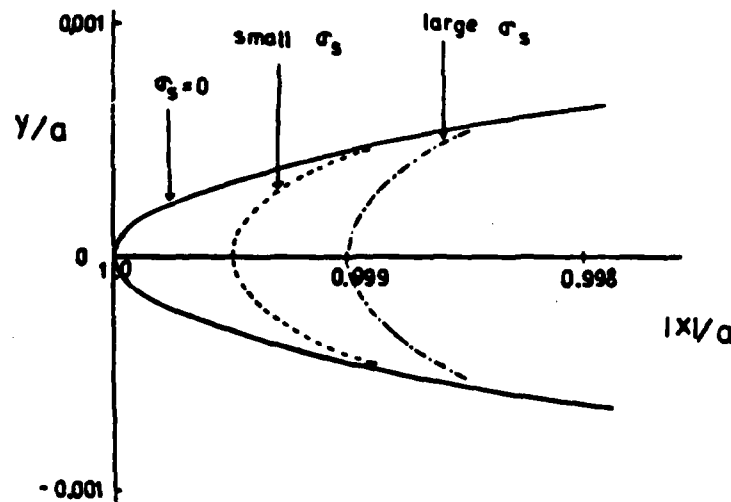


Fig. 3. Schematic diagram of crack tip geometry variation by surface energy variation. Elliptic crack with  $a/b = 100$  is shown. Large  $\sigma_s$  corresponds to the case in vacuum and small  $\sigma_s$  corresponds to the case in water.



## DISCUSSION

In all of the three mechanisms considered, the surface energy  $\sigma_s$  tends to increase the mechanical strength of glass. Reducing this quantity by liquids such as water will reduce the strength. Also the maximum strength should be realized for a given material, when  $\sigma_s$  is the maximum, which can be probably attained in vacuum. The smaller reduction of  $\sigma_s$  in organic liquids than in water leads to the higher strength in these liquids than in water.

Although there is an uncertainty in the real magnitude of the surface energy effect, because of the unknown crack tip geometry, the present result, together with the abundant experimental evidences, indicates the importance of the surface energy in the fracture strength of brittle materials.

## CONCLUSIONS

Equations for the strength of the brittle material have been modified to incorporate the effect of the surface energy variation by environment. The result shows that the strength decreases with the decrease of the surface energy, consistent with the experimental observation.

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